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ELECTROCAPILLARYPHORESIS, A POTENT CAUSE OF DESORPTION PEAKS AND POLAROGRAPHIC MAXIMA

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The effect of surface active substances on the differential capacity of a dropping mercury electrode was first reported by Frumkin and Proskurnin.[1] They showed that the surface active substance depresses the capacity of the dropping mercury electrode at the electrocapillary zero. Furthermore, they observed that at certain potentials on either side of the electrocapillary zero, there is an abrupt increase in the differential capacity, which is referred to as the desorption peak.

The depression in the capacity has been established as due to the strong adsorption of the surface active substance. The adsorption is mainly caused by the tendency on the part of the hydrophobic group of surface active substances to get away from water.[2] This has been aptly referred to as squeezing type of forces by Grahame.[3] The hydrophobic group finds itself in a relatively high potential energy state within the network of hydrogen bonds in the aqueous media. The hydrophobic group therefore tries to get out of the water and gets adsorbed on the dropping mercury electrode. This adsorption takes place unhindered at the electrocapillary zero. At potentials sufficiently removed from the electrocapillary zero, the intensely charged mercury surface would attract the water dipoles preferentially, which would lead to desorption of the surface active substance. The desorption is found to occur rather abruptly at well-defined potentials, characteristic of the system.

It has to be pointed out, however, that the occurrence of the peak at the desorption potential is yet to be explained. The desorption should have normally raised the capacity to that obtained with pure indifferent electrolyte; actually, however, the peak capacity at desorption potential attains a value which may be several hundred per cent. higher than the capacity with the pure indifferent electrolyte at that potential. The enormous peaks in the differential capacity observed have been explained as produced by the excursions of the potentials due to the superimposed A.C. ripple causing sorption and desorption processes, which are supposed to

cause a high dynamic capacitance. This explanation has been accepted by all the workers so far.

With a view to elucidate further this phenomenon, the effect of stirring on differential capacity of the dropping mercury electrode was studied. The experimental set-up was nearly the same as used by Doss and Gupta.[4] The voltage drop resistor was kept constant at 200 Ω. The Philips GM 6017 Vacuum Tube Voltmeter was used as an amplifier, and the amplified current was rectified and measured by a galvanometer with a suitable shunt. Since the resistive impedance of the rest of the circuit was low as compared with the impedance due to the capacity of the dropping mercury electrode, the galvanometer deflections were nearly proportional to the differential capacity. The other details of the experimental set-up are as follows:—

$m = 0{\cdot}936$ mg. per sec.

$t = 5{\cdot}8$ sec. per drop in 0·1 M KCl, open circuit.

$h = 63$ cm. of mercury.

A.C. ripple = 30 mV. (r.m.s.); 50 cycles.

D.C. potentials are with reference to saturated calomel electrode.

Indifferent electrolyte = 0·1 M — KCl.

1 μA (r.m.s.) = 30 divisions of galvanometer deflection.

The galvanometer deflections give the electric double layer capacity in arbitrary units.

Surface active substance = sodium dioctylsulphosuccinate ("Manoxol-OT" of "100 per cent." quality kindly spared by the Imperial Chemical Industries).

It was observed that the capacity at desorption potential, on stirring, rose up and gave nearly the same value of the capacity, irrespective of the concentration of the surface active substance and nearly equal to that which was got with the pure indifferent electrolyte under stirred conditions. For example at a potential of $-1{\cdot}35$ V. (*vide* Fig. 2), it is seen that the capacity increases from 95 to 203 units. Similarly at the same D.C. voltage in the case of the pure indifferent electrolyte (Fig. 1), it rises to about 210 units. This interesting feature indicated to us that the surface active substance may be bringing out a stirring effect at the desorption potential.

Accordingly this aspect was further investigated. In order to examine whether any movements occur at the mercury-aqueous interface, a narrow strong beam of light from an arc lamp was directed to the dropping mercury

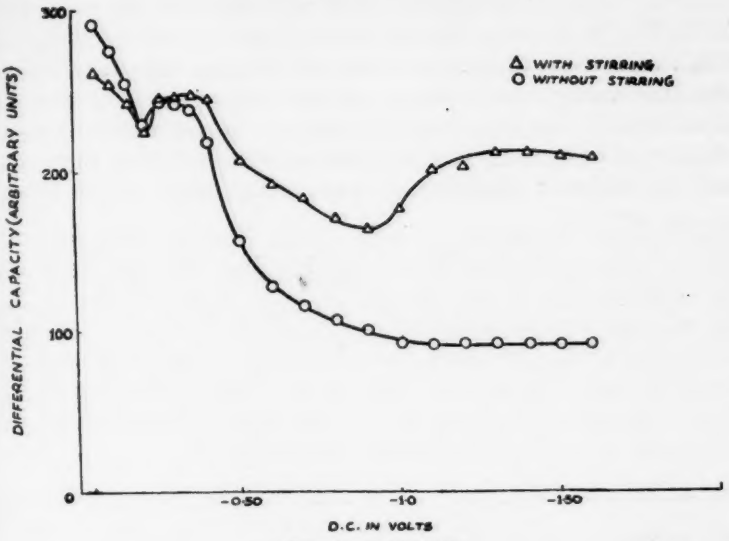

FIG. 1. 0·1 M KCl.

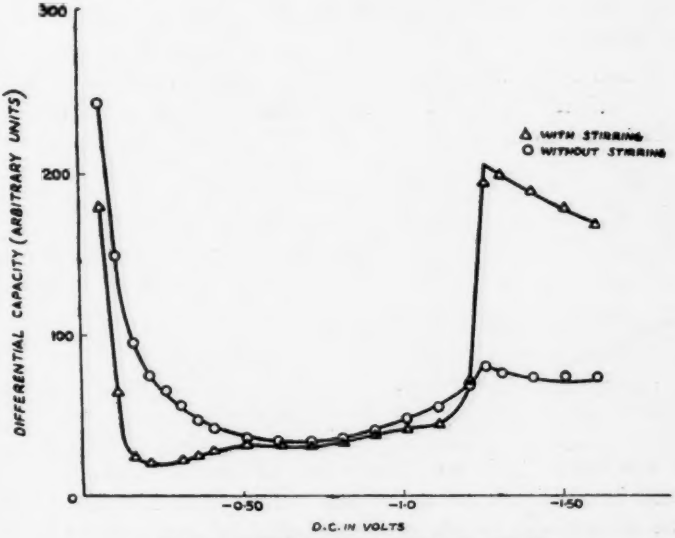

FIG. 2. 0·0025% Manoxol-OT in 0·1 M KCl.

electrode and observations were made at right angles to the beam through a microscope. A small amount of fine talc powder was added to render the liquid movements visible. A careful examination showed that vigorous directed movement of the liquid was occurring at the mercury drop in the neighbourhood of the desorption potential. It was also further observed that the directed movement was much less at other potentials corresponding to small capacities of the dropping mercury electrode.

The directed movement of liquid at the dropping mercury electrode known to occur at polarographic maxima, was first discovered by Antweiler[5] by his carefully designed schlieren technique. It is now shown by us that similar vigorous directed movement occurs at the desorption peaks of the tensammetric curves. We have also observed that the movement is not dependent on the presence of the A.C. ripple. The results bring out clearly that this movement is a major, if not the sole, factor in producing the desorption peak and especially in enhancing its abruptness.

Antweiler[5] and Stackelberg[6] rightly attributed the polarographic maxima as having been caused by these directed movements. The directed movement at mercury drop was, however, interpreted by Antweiler[5] as due to the electrokinetic effects. This is not probable, as the movements are extremely fast and the potential gradients involved are comparatively of a low order. Doss[7] and Stackelberg[8] rightly attributed the movement to the differences in the interfacial tension at the different portions of the mercury drop. To account for these differences in the interfacial tension, Stackelberg postulated that they are caused by the shielding effect of the capillary, leading to the establishment of different potentials at the different points on the aqueous side of the mercury-aqueous interface. He took the analogy from the observations that he made with his experiments on the mercury pool and the large stationary drops.[6, 8] It has to be pointed out, however, that his experiments with large pool of mercury and stationary drops dealt with comparatively large currents and large voltage drops in the solution. In view of this, large differences can occur in the potential at the different points on the aqueous side of the mercury-aqueous interface of the extensive mercury surfaces dealt with. It appears to the present authors, however, that such large differences in potential cannot be caused by the current passing under conditions of polarography, due to the facts that (*a*) the mercury drops are extremely small in size, (*b*) the aqueous solutions are highly conducting and (*c*) the currents met with are small. This is especially true of tensammetric curves, wherein the currents involved are extremely small since only condenser currents exist. It is to be pointed out in this connection that in tensammetric experiments

the movements persist even in the absence of the A.C. ripple when the D.C. current passing is a small fraction of a micro-ampere. The potential differences caused by the shielding effect would, therefore, be negligible. This is further confirmed by the fact that the occurrence of the polarographic maxima as well as the desorption peaks is practically independent of the distance of the dropping mercury electrode from the pool electrode.

The present authors, on the other hand, consider that the explanation given by Doss and Kalyanasundaram[2] for the differences in the interfacial tension at the dropping mercury electrode, is more plausible. According to them the *fresh* mercury surface emerging out of the capillary which has its interfacial tension corresponding nearly to that of electrocapillary zero, takes finite time before it attains the proper value of the interfacial tension by interacting with the aqueous solution and the potential existing. The mercury drop, therefore, would have different interfacial tensions at different portions of the drop. These differences however can be large or small according to the circumstances. In the polarographic maximum exhibited by a reducible ion, it is the slowness of the electrode reaction at the half-wave potential that is mainly responsible for the differences in the interfacial tension at the different parts of the mercury drop. These differences therefore get eliminated once the reaction is made faster by raising the potential sufficiently to a more negative value. This explains how proper concentration polarisation occurs at higher negative potentials whereas near the half-wave potential peak-like maximum occurs. Furthermore, at the maximum of the electrocapillary curve, the differences in the interfacial tension would practically vanish; this explains why no polarographic maximum is observed near the electrocapillary zero. The presence of sufficiently high concentrations of adsorbable surface active substances would also help in reducing the differences in the interfacial tension at the different points on the mercury drop. This explains the action of the surface active substances as inhibitors of polarographic maxima.

The same explanation also holds good in the case of desorption peaks. At the desorption potential due to the differences in the state of adsorption of the surface active substance at the different portions of the drop (caused by the time taken for the electro-chemical and adsorption equilibria), large differences in the interfacial tension arise and give rise to the vigorous directed movements.

We would, therefore, emphasise *that the polarographic maxima as well as the desorption peaks in tensammetric curves are caused by electrocapillary-*

phoretic movements which are in their turn caused mainly by the effect of fresh surface emerging from the capillary tip.*

The observation of electrocapillaryphoretic movements, although to a lesser extent at other potentials, brings out clearly a neglected factor which is of importance in interpreting the data obtained in such systems. The dropping mercury electrode is normally preferred to a mercury pool or a stationary drop in view of the fact that in the former case one deals with a fresh surface of mercury and the interference by the surface active impurities would be negligible; but the observations made in this paper indicate that great caution should be exercised in interpreting the data obtained from the dropping mercury electrode. *These observations are therefore of profound significance and lead to the conclusion that one should make sure in every case that the electrocapillaryphoretic movements are negligible before any quantitative interpretation is given to the data obtained with the dropping mercury electrode.*

Summary

The effect of sodium dioctysulphosuccinate on the differential capacity of dropping mercury electrode in 0·1 M KCl solution is studied. It is observed that at the desorption potential, vigorous directed movement of liquid occurs at the mercury-aqueous interface. This movement is shown to be responsible for the desorption peak in the differential capacity-potential curve.

The cause of the directed movement is further examined. Arguments are given to support the ideas of Doss and Kalyanasundaram, that the movement is caused by the emerging surface of mercury having a different interfacial tension from that of the older surface, and that the shielding effect of the capillary postulated by Stackelberg does not appear to play an important part either in the production of the desorption peak or the polarographic maxima.

It is found that the directed movement of liquid occurs although to a less extent at potentials far removed from the desorption potential. This result is of great significance in that it points at the importance of looking for such movements before interpreting quantitatively the data obtained with a dropping mercury electrode.

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* Doss[7] observed similar movements at mercury pool when alternating current is incident and termed the phenomenon as *Electrocapillaryphoresis* since the movements are caused by electrocapillary effects.

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STUDIES ON COLLAGEN

III. Oriented Crystallisation of Inorganic Salt on Collagen*

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I. Introduction

During studies made in this laboratory on the effect of alkali on collagen, it was found that the treated fibres showed, in addition to the collagen wide angle pattern, a large number of reflexions arranged along layer lines. A similar observation had been made by Clark and Schaad (1936) who supposed that these reflexions were produced by addition compounds of collagen with alkali. While the photographs reported by Clark and Schaad contained only a few spots in addition to those of collagen, the patterns obtained by the author contained a series of them extending over the whole range of 2θ.

A careful study of the photograph revealed the remarkable fact that the extra reflexions were caused by sodium carbonate monohydrate (Na_2CO_3, H_2O) rotated about its *b*-axis. Thus it appeared that the phenomenon was not one of addition compound formation but of oriented crystallisation on collagen. The study was therefore extended to various other soluble salts. A number of salts were found to crystallise well in the fibre even though the solutions employed were far from being saturated and there was no crystallisation in the mother liquor itself. On the other hand, some salts failed to crystallise inside the collagen. The nature (phase) of the deposited crystallites was also found to vary considerably with the pH of the solution employed. The study was later extended to feather keratin, another fibrous protein believed to possess structural similarity with collagen. In this case also, oriented crystallisation was found to occur. This paper deals with the experimental study made on collagen.†

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* A portion of this paper has been taken from the thesis accepted by the University of Madras for M.Sc. Degree.

† A part of the work was actually completed in 1954 and a preliminary note was published in 1955 (Ramachandran and Ambady, *Experientia*, 1955, **11**, 343). Recently it has come to the notice of the author that similar studies were carried out by Zaides (1950), who had also attributed the observed elongated arcs to the adsorbed crystallites of the salt used in solution.

2. Experimental Details

The investigation may be divided into two parts. During the first stage, experiments were performed with solutions of sodium and potassium hydroxide of strength about 0·25 N. The results obtained from these experiments led to the establishment of the phenomenon occurring as oriented crystallisation. In the second stage, alkaline, neutral and acidic solutions of a large number of simple inorganic salts were employed. Fibres of knagaroo tail tendon and " tendo achilles " of horse were used throughout. The solutions were kept in open dishes and the fibres were soaked in them for periods ranging from 16–20 hours. The treated fibres did not exhibit any external change.

However, when viewed under the polarising microscope, the specimens in which oriented crystallisation had taken place were found to possess strong birefringence. The X-ray patterns of the dried specimens were recorded as usual in conventional cylindrical and flat plate cameras, using Cu Kα radiation.

3. Results

(*a*) *Sodium and potassium hydroxide.*—Fibres treated with sodium hydroxide yielded two types of X-ray patterns. They are reproduced in Figs. 1 and 2 and will hereafter be called NaOH-I and NaOH-II respectively. Even on a cursory inspection, it was evident that the pattern of NaOH-I and that of the sodium addition compound reported by Clark and Schaad were caused by one and the same substance. According to these authors the substance belonged to the orthorhombic system with the cell dimensions $a = 5{\cdot}32$ Å, b (fibre axis) $= 6{\cdot}50$ Å and $c = 11{\cdot}90$ Å. From measurements made on the X-ray diagram of this compound (NaOH-I), the ξ-values of all the *extra* reflections were calculated. By trial it was found that the calculated values of ξ^2 fitted into an orthorhombic cell of dimensions, $a = 10{\cdot}1$ Å, b (fibre axis) $= 6{\cdot}45$ Å and $c = 5{\cdot}30$ Å. It may be noticed that two of the parameters are practically same as those calculated by Clark and Schaad for their addition compound, while the third is definitely different. The cause of the discrepancy is due to the fact that the above authors have also taken into consideration the equatorial reflexions of the wide angle pattern of collagen. The cell dimensions calculated for NaOH-I ruled out sodium hydroxide as the substance causing the extra reflexions, as they did not agree with the reported data on any of the forms of solid NaOH. It then occurred to the author that the deposit could possibly be a carbonate of sodium formed by the action of atmospheric carbon dioxide on the alkali. A survey of the known structures of various sodium carbonates revealed

that the cell dimensions of Na_2CO_3, H_2O were very nearly equal to above calculated values (orthorhombic, $a = 10{\cdot}72$ Å, $b = 6{\cdot}44$ Å and $c = 5{\cdot}24$; Wyckoff, 1951). Moreover the ξ^2-values obtained from NaOH-I photograph and those calculated from the data given by Harper (1936) agreed very well. This proved beyond doubt that the extra reflexions were due to the crystalline modification Na_2CO_3, H_2O.

Since both NaOH-I and NaOH-II were prepared under identical conditions, it was reasonable to assume that the deposited substance in the latter case also was some other carbonate of sodium. This was further strengthened by the fact that the layer spacing along fibre axis measured 3·48 Å—a value very close to the *b*-parameter of sodium sesquicarbonate (Na_2CO_3, $NaHCO_3$, $2\,H_2O$; monoclinic, $a = 20{\cdot}41$ Å, $b = 3{\cdot}49$ Å, $c = 10{\cdot}33$ Å and $\beta = 106° 20'$). Making use of the data given in the original paper, (Brown, Pieser and Turner Jones, 1949) ξ^2-values of strong reflexions were calculated and were compared with the experimental values obtained from the NaOH-II photograph. The two sets of values were found to agree remarkably well.

As in the case of sodium hydroxide, two different X-ray diagrams (referred to hereafter as KOH-I and KOH-II) were recorded with fibres treated in potassium hydroxide also. The deposit in KOH-I was identified as potassium bicarbonate. The crystallites were found to be oriented with their *c*-axis (3·71 Å), lying along the fibre axis. It may be noted that Clark and Schaad had wrongly ascribed to the same substance (which they called potassium addition compound) a monoclinic cell of dimensions $a = 4{\cdot}28$ Å, b (fibre axis) $= 3{\cdot}78$ Å, $c = 14{\cdot}1$ Å and $\beta = 59° 45'$. Those for $KHCO_3$ (Nitta, Tomie and Koo, 1952) are $a = 15{\cdot}11$ Å, 5·67 Å, $c = 3{\cdot}71$ Å and $\beta = 103° 45'$ of which the spacing along the fibre axis alone agrees with the parameter given by the authors.

In the case of KOH-II, the orientation was poor, as indicated by powder rings. The substance was identified to be $2\,K_2CO_3$, $3\,H_2O$ from the A.S.T.M. cards. Some of the strong lines observed in the X-ray diagram were found to be common to both potassium carbonate hydrate as well as to potassium hydroxide. It was possible that the deposit contained KOH also, in addition to $2\,K_2CO_3$, $3\,H_2O$, though it is difficult to explain how KOH could have existed in a pure form in the fibre even after several days of exposure to the atmosphere.

Fibres treated with freshly prepared solutions of the two hydroxides kept in sealed vessels failed to exhibit any oriented crystallisation. This

result clearly showed that the crystallising compound, namely the carbonate, was formed in the solution and not in the fibre by chemical action.

(*b*) *Reactions with other salts.*—Fibres treated with a saturated solution of copper sulphate gave only the wide angle pattern. However, the X-ray diagram of a fibre treated in alkaline solution exhibited a large number of extra reflexions arranged along regular layer lines (Fig. 3). The layer line spacing measured 7·0 Å, a value close to the *c*-spacing of sodium sulphate-III (orthorhombic, $a = 5{\cdot}59$Å; $b = 8{\cdot}93$ Å and $c = 6{\cdot}98$ Å). Knowing the cell parameters and the space group of this substance (Frevel, 1940) ξ^2-values of the permitted reflexions were calculated. The identification was now carried out as in the previous cases, by comparing the observed and calculated ξ^2-values.

However, experiments performed with *neutral* solutions of sodium sulphate failed to give any oriented crystallisation of the salt. So also, neutral solutions of sodium tartrate and sodium carbonate gave negative results.

Experiments were now conducted with alkaline solutions of a number of inorganic salts (Table I). The X-ray diagrams recorded with the fibres treated with sodium fluoride, sodium bicarbonate and sodium tartrate are given in Figs. 4, 5 and 6.

An attempt was then made to understand why some salts crystallised readily in collagen while others failed to do so. When the value of the parameter (p) of the crystallising salts which was parallel to fibre axis was carefully examined in the successful cases, a remarkable discovery was made namely that the product of this parameter with a simple integer (N) always took a value between 27·5 Å and 29·5 Å. In fact, when the value of product (Np) exceeded 29 Å, the meridional spacing of the collagen was found to increase from the normal value of 2·88 Å to as much as 2·95 Å in certain cases. These considerations indicated that the mechanism attending oriented crystallisation was essentially one of epitaxial growth, in which one of the crystal axes gets oriented parallel to the fibre axis. Then it is understandable that the lattice of the substrate would extend slightly to accommodate crystallites of a larger parameter. [It was incorrectly stated in the earlier note (Ramachandran and Ambady, 1955) that the cell parameter concerned always assumed a value between 3·2 and 3·75 Å or a multiple of this.] In the case of salts which gave negative results, it was found that the value of the product Np, with the exception of potassium iodide, potassium sulphate, potassium chlorate and potassium chloride, always lay beyond the two limits. The powder rings observed in the X-ray diagram recorded with tendon treated

TABLE I

Substance	Cell parameters (Å)				Nature of crystal growth	Parameter parallel to fibre axis (p)	Value of Np	Value of meridional arc	N
	a	b	c	β					
Na_2CO_3, H_2O	10·72	6·44	5·24	..	Good	6·44 (b)	28·92×2	2·92	9
Na_2CO_3, $NaHCO_3$, $2H_2O$	20·41	3·49	10·31	106° 20′	Good	3·49 (b)	27·92	2·88	8
Na_2SO_4-III	5·59	8·93	6·98	..	Good	6·98 (c)	27·92	2·88	4
$Na_2C_4H_4O_6$	11·49	14·67	4·97	..	Misoriented layer lines	4·97 (c)	29·82	2·95	6
NaF	4·62	..	..	..	Powder lines	4·62	27·92	2·88	6
NaCl*	5·63	..	..	..	Powder lines	5·63	28·15	2·88	5
$NaHCO_3$	7·51	9·70	3·53	93° 19′	Misoriented layer lines	3·53 (c)	28·24	2·88	8
$KHCO_3$	15·11	5·67	3·71	103° 45′	Poor	3·71 (c)	29·68	2·92	8
KNO_3	5·43	9·17	6·45	..	Poor	6·45 (c)	29·0×2	2·92	9
$KClO_3$	4·65	5·59	7·09	109° 58′	Poor	4·65 (a)	27·90	2·88	6
K_2SO_4	10·01	7·42	5·73	..	Poor	7·42 (b)	29·6	2·92	4
$2K_2CO_3$, $3H_2O$	..	..	..	..	Powder lines	5·73 (c)	28·5	2·88	5
KOH	..	..	..	..	Powder lines	..	..	..	..
RbCl	6·54	..	..	..	Powder lines	6·54	29·68	2·92	9
CsI	4·56	..	..	..	Negative	..	31·0, 27·4	..	..
RbBr	6·86	..	..	..	Negative	..	27·4, 34·3	..	..
KCl	6·27	..	..	..	Negative	..	28·2×2	..	9
KI	7·05	..	..	..	Negative	..	28·20	..	4
K_2TeO_4, $2H_2O$	6·27	6·1	12·13	109° 13′	Negative	..	31·4, 30·5	..	5, 5

* Recently NaCl has been found to exhibit parallel growth with good orientation on a fibre swollen in *m*-cresol.

with potassium iodide did not fit in with known compounds of potassium. The iodide itself did not crystallise, but it may be mentioned that this compound has a lyotropic action of collagen, leading to a breakdown of its structure.

(*c*) *Studies at different pH's.*—It was not clear at this stage why some salts failed to exhibit oriented crystallisation, in spite of the excellent geometric fit available. Since the solutions used in this set of experiments were fairly concentrated, the only other factor which could have inhibited crystal growth was probably the pH of the solution. Detailed experiments conducted with sodium sulphate, potassium sulphate and potassium chlorate showed that oriented crystallisation occurred when the pH of the solution was between 2·2 and 2·4 and between 12 and 13. The X-ray diagrams obtained with fibres treated in acid solutions of potassium sulphate and sodium sulphate are reproduced in Figs. 7, 8 and 9 respectively. It may be observed that the misorientation as well as the particle size of the deposit increases as the pH goes above 2·3 (Figs. 8 and 9). In the alkaline solution of low pH the deposit gave only powder lines. In alkaline pH, another form of sodium sulphate namely thenardite (A.S.T.M. card No. 5·0631) was also found to occur. In the case of potassium sulphate, the crystallites were deposited with both *b* and *c* parameters lying along fibre axis. The X-ray diagram presented here shows the *c* orientation. Potassium chlorate was deposited on the fibre from alkaline solutions with its *a*-axis (4·65 Å) parallel to the fibre axis. Deposition of the salt occurred also in solutions of pH 2·4, but due to extreme misorientation no definite layer line could be observed. In general, it was found that the orientation of potassium salts was considerably lower than that of sodium salts.

As all the salts used in this study were highly soluble, washing the fibres with distilled water even for a short time completely removed the deposited crystallites. However, it must be mentioned that in experiments conducted on deposition of calcium phosphates on collagen the deposit could not be removed by washing. Stretching the fibre before treatment with various solutions produced marked improvement in the orientation of the deposited crystallites.

4. Discussion

Epitaxis is a well-known aspect of crystal growth. Though considerable researches have been carried out on the phenomenon, most of it is confined to two-dimensional overgrowth on crystalline substrates. Exhaustive accounts on the subject are given by Van Der Merwe (1949) and Buckley

* Recently NaCl has been found to exhibit parallel growth with good orientation on a fibre swollen in *m*-cresol.

(1951). On examining the experimental results obtained with collagen, one finds that in almost all cases there exists a geometric fit between the axial repeat of collagen and the overlapping parameter of the deposited salt.

Now the axial repeat of the collagen is believed to be 28·6 Å (Ramachandran and Kartha, 1955). In the helical structure of collagen the only repeating unit is the axial repeat. Hence the molecule may be considered as a one-dimensional substrate, on which parallel growth can occur only along the fibre axis. Since a crystallite can get attached to any point on the surface of the protofibril, there will be complete random orientation among the deposited crystallites in directions at right angles to the fibre axis. Therefore the X-ray diagram of the treated fibre would resemble a single crystal rotation photograph of the particular substance, taken about the axis which is aligned parallel to fibre axis. An examination of column 5 of Table I reveals that in all cases the value of Np is in complete agreement with the repeat of collagen, namely 28·6 Å. However, in a few cases, as for example KCl (Np = 28·2 Å), negative results were obtained. Such negative results are reported in the literature on epitaxis. They have been ascribed to the failure to form chemical bonds between corresponding units on the substrate and deposits.

In collagen, charged centres are available in the form of basic and acidic amino acid side groups which project outwards from the back bones of the polypeptide chains. These groups are believed to occur at definite levels along the fibre axis though the actual distribution is not known. In acid and alkaline solutions, the intermolecular bonds of collagen are weakened or even ruptured giving rise to swelling of the fibre. The degree of swelling is found to vary with the pH of the solution used. This is clearly indicated by the titration curve for collagen (Bowes and Kenton, 1948) which shows a peak at about pH 2·2. Swelling is minimum in neutral pH while in alkaline solutions, it increases rapidly above pH 10. Hence when collagen fibres are placed in salt solutions whose pH is adjusted to that corresponding to a large swelling, the solutions enter into the fibre. When the specimen is removed from the solution, water evaporates off and the dissolved salt crystallises in the interstices between the fibrils in the specimen. It is reasonable to suppose that the charged groups on the molecule which project out of the surface of the fibrils must be playing an important part in determining the orientation of the crystallites along the fibre axis.

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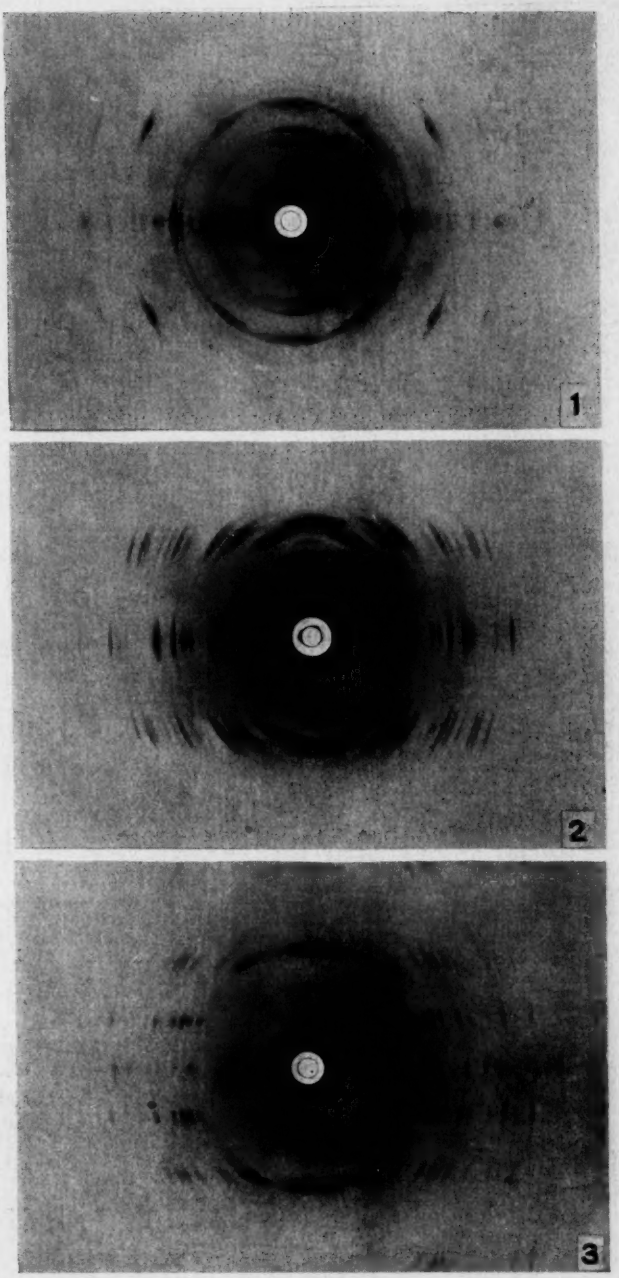
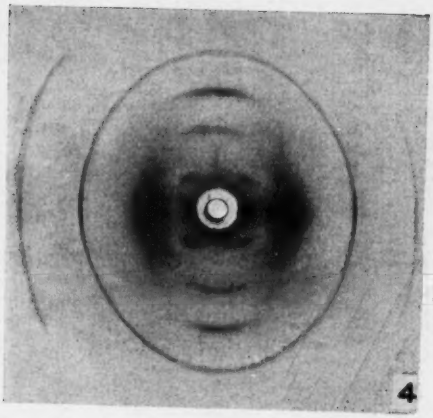
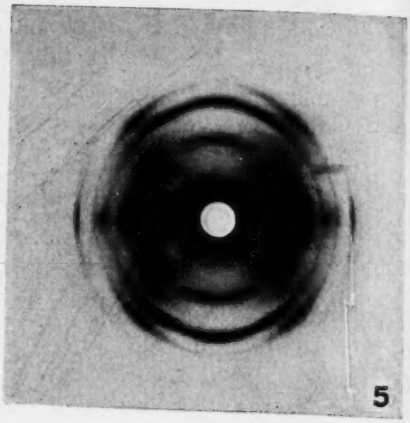
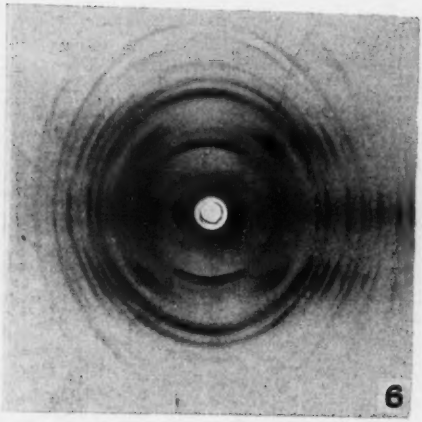
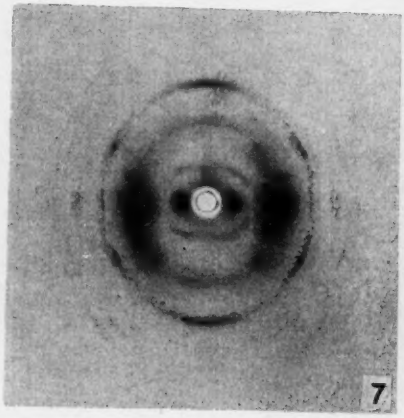


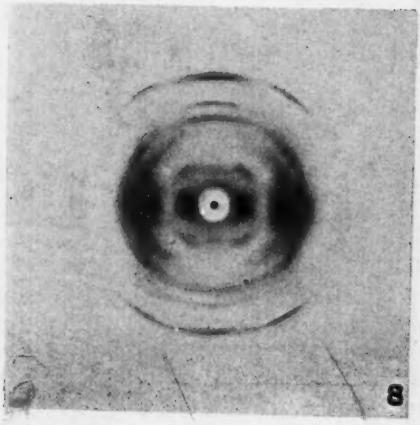
FIGS. 1–3

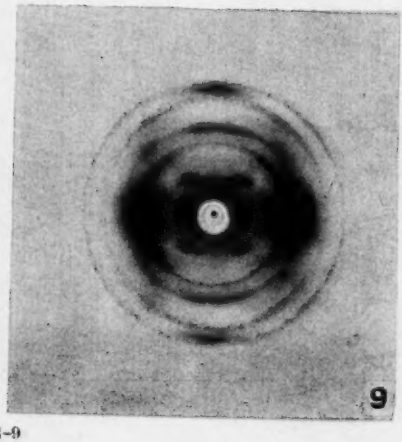












FIGS. 4–9

Dr. D. Ramaswamy of the Central Leather Research Institute, Madras, for help in the chemical measurements and to the University of Madras, for the award of a studentship.

Summary

When collagen fibres are treated with acidic and alkaline solutions of inorganic salts, oriented crystallisation of the salts takes place inside the protein fibre. The treated fibres give X-ray diagrams which closely resemble single crystal rotation photographs. A direct relationship has been established between the crystal parameters lying parallel to the fibre axis and the axial repeat of collagen. Oriented crystallisation does not occur in neutral solutions. In both acidic and alkaline solutions the orientation improves with swelling. The chemical treatment is found to have little effect on collagen itself in most of the salts.

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Description of Plates

(All photographs except Figs. 8 and 9 were taken in cylindrical camera of radius 3 cm.).

Plate IV

Fig. 1. Sodium carbonate, monohydrate.

Fig. 2. Sodium sesquicarbonate.

Fig. 3. Sodium sulphate-III.

Plate V

Fig. 4. Sodium fluoride.

Fig. 5. Sodium bicarbonate.

Fig. 6. Sodium tartrate.

Fig. 7. Potassium sulphate.

Fig. 8. Sodium sulphate (Flat plate, D = 3 cm.) at pH 2·3.

Fig. 9. Sodium sulphate (Flat plate, D = 3 cm.) at pH about 3·0.

INFLUENCE OF SURFACE ACTIVE AGENTS ON SPECTROPHOTOMETRIC DETERMINATIONS OF pH

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Introduction

pH of a solution containing an indicator and surface active agent when determined colorimetrically shows an apparent shift from the true Sorenson value. Smith and Jones,[1] Hartley[2] and Roe[3] have in the past studied this phenomenon qualitatively. They also tried to correlate the effect with valence change in indicators and the cataphoretic mobility of the micelles formed by paraffin chain salts used as wetting agents. Later Krishnappa *et al.*[4] tried to apply the law of mass action to the complexes formed by the wetting agents with the indicators. They thus postulated a quantitative approach according to which

$$-\Delta \text{ pH} = \log \frac{1 + k_2 C_w}{1 + k_1 C_w}$$

where k_1 and k_2 are the stability constants for the complexes formed by the wetting agent with the indicator and C_w is the concentration of the wetting agent. Their experiments using Igepon-T agreed with the above relation whereas Nekal-BX showed large deviations. However, a literature survey indicated that during the last 10, 12 years not much further work has been done in this direction and that the above equation has not been applied to the large number of other wetting agents now known. It was, therefore, considered worthwhile to study the effect of a few more wetting agents on thymol blue itself in acid solutions and the results are reported in this paper.

Experimental

Manoxol-OT (a B.D.H. product, 100% Aerosol-OT), Teepol and Dodecyl benzene sodium sulfonate (active constituent of Stanvac detergent 4OE) have been used in this work.

The Stanvac detergent 4OE (containing 38% of dodecyl benzene sodium sulfonate and balance mostly sodium sulfate with small percentage of phosphate and sodium chloride) was extracted with methanol (GR), filtered and

the filtrate evaporated to dryness over a steam-bath. The residue was obtained as an yellowish-white soapy solid. The methanol extraction was repeated to remove all the inorganic sulphate and chloride and the residue thus obtained was used in the work.

A 0·04% solution of thymol blue is prepared by dissolving the solid indicator (Mercks GR quality) in 0·5 c.c. of N NaOH and making up with water.

UNICAM SP 600 spectrophotometer was employed to determine the ratio of the concentrations of the basic to acidic form of the indicator present in the test solution. The apparent pH was calculated from the equation

$$\text{pH} = pk - \log \frac{a_b - a_x}{a_x - a_a}$$

where a_b, a_x and a_a are the absorbancies of the basic standard, the test solution and the acid standard respectively. The standards used were the following ones:—

Acid standard.—2·5 c.c. of 0·04% solution of thymol blue + 36·65 c.c. of N HCl; made up to 50 c.c. (the Sorenson value of this solution was found to be about 0·494).

Basic standard.—2·5 c.c. of 0·04% solution of thymol blue + 10 c.c. of buffer of pH 4·95; made up to 50 c.c.

Test solution.—To 2·5 c.c. of 0·04% solution of thymol blue, appropriate amounts of sodium acetate and hydrochloric acid were added to get the required pH when made up to 50 c.c. But, before making up different volumes of a solution of wetting agent (WA) were added to give the required concentration when finally made up to 50 c.c. with water.

The Sorenson values of test solutions and standards were determined by the quinhydrone method using an OSAW potentiometer and a multiflex galvanometer with a sensitivity of $4{\cdot}45 \times 10^{-9}$ A/mm.

Results and Calculations

A set of experiments, with varying amounts of 0·60% solution of the Manoxol-OT, was carried out with potassium chloride and hydrochloric acid buffer of pH 2·0. It was noted that some experimental solutions, particularly at higher concentrations of WA are not absolutely clear and hence only concentrations below 0·4% of WA were reported. The absorbancies of all the solutions were measured at a wavelength of light = 543 $m\mu$, corresponding to maximum absorption as found by studying the absorption spectrum of thymol blue in the acid standard.

In order to compensate for the light absorption characteristics due to the turbidity alone, the percentage transmissions of blank solutions, *i.e.*, solutions exactly similar to the test solutions but without the indicator being present, were measured separately. The difference between the percentage transmission of water and each of the above blank solutions (buffer + wetting agent) was found out and added on to the percentage transmission of the test solution (buffer + wetting agent + indicator), thus making good the error due to the turbidity, provided it is simply additive and does not produce other complications. The apparent Δ pH values (the difference between the Sorenson value and the pH by spectrophotometric method) as calculated from such corrected data do not appear to vary regularly with increasing amounts of the wetting agent (Table I, Column 3). Other corrections were therefore applied.

Normally acid standard, as used for such purposes should have a pH = $pk - 2$. But as the pk value for thymol blue is 1·7,[5] no such acid standard is practicable. Further, it would be seen that the acid standard initially used by us as well as Krishnappa *et al.* had a pH of about 0·5 or more. But when the wetting agent is present the apparent pH is diminished to a value roughly equal to $pk - 2$, thereby compensating and giving an absorbance value which may be taken as a_a. It is on account of this factor that Krishnappa *et al.* could get coherent results even when using an acid standard solution of pH as high as 0·5–0·7. The same procedure was adopted by us also and gave reasonable results at low concentration of wetting agent (WA 0·02%). However, when higher concentrations of WA were used to make up the acid standards, they became turbid and so this method of compensation could not be applied. The a_a value for pure acid standard free of WA also did not lead to satisfactory results as Δ pH became imaginary as a_x, often came out to be greater than a_{a_2}. In order to apply the necessary correction, therefore, a theoretical value of a_a was computed as shown below:—

pH (Sorenson value) of the acid standard $= 0{\cdot}4942$

The absorbance of the acid standard (observed) $a_a = 1{\cdot}4500$

The absorbance of the basic standard $= 0{\cdot}0375$

$$\text{pH} = pk - \log_{10}\frac{\text{HA}}{\text{A}}$$

$$0{\cdot}4942 = 1{\cdot}7 - \log_{10}\frac{\text{HA}}{\text{A}}$$

$$\therefore \quad \log\frac{\text{HA}}{\text{A}^-} = 1{\cdot}7 - 0{\cdot}4942 = 1{\cdot}2058$$

TABLE I

a_a (Corrected)	= 1·5380
a_b	= 0·0375
pH (Sorenson Value) of the acid standard	= 0·4942

Conc. of WA	Manoxol OT				Dodecyl benzene sodium sulfonate			
	Ionic St. ·5		Ionic St. ·02		Ionic St. ·02		Ionic St. ·2	
	pH by QH	Δ pH by spectro-photometer	pH by QH	Δ pH by spectro-photometer	pH by QH	Δ pH by spectro-photometer	pH by QH	Δ pH by spectro-photometer
1	2	3	4	5	6	7	8	9
·39	1·93	−0·19	2·68	−0·98	3·12	−2·26	..	..
·30	1·91	−0·24	2·74	−0·81	3·11	−2·13	2·33	..
·20	1·91	−0·44	2·71	−0·60	2·97	−1·88	2·33	−1·84
·15	1·90	−0·415	2·64	−0·52	3·02	−1·86	2·31	−1·84
·10	1·87	−0·17	2·58	−0·23	3·02	−1·63	2·31	−1·60
·08	1·85	−0·15	2·78	−0·15	3·06	−1·51	2·31	−1·52
·05	1·80	+0·12	2·62	+0·20	3·04	−1·00	2·31	−1·25
·02	1·76	+0·45	2·58	+0·36	2·99	−0·39	2·31	−0·57
·00	..	..	2·81	..	..	..	..	..

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or

$$\frac{HA}{A^-} = 10^{1\cdot2068} = 16\cdot06$$

$$\therefore \quad 16\cdot06 = \frac{a_b - a_x}{a_x - a_a},$$

Substituting the value of a_a (obs.) for a_x

i.e., $$16\cdot06 = \frac{0\cdot0375 - 1\cdot450}{1\cdot450 - a_a}$$

i.e., a_a (corrected) $= 1\cdot5380.$

It is interesting and reassuring to see that the a_a value both by the addition of WA (0·02%) to acid standard and by calculation comes to be very nearly the same, although at higher concentration of WA this is disturbed by the turbidity effect. This theoretical and corrected value of a_a was employed in calculating Δ pH in the above set of experiments. However, when in spite of this correction, the apparent pH shifts experimentally obtained with manoxol-OT were not found to be coherent, it was surmised that the turbidity effect might not be simply additive, but interfering in nature. Hence, another method of applying the turbidity correction was tried. This was based on the theory of isobestic point at which each indicator has the same absorbance irrespective of pH. It was, therefore, thought that the pH shifts and the resultant colour changes will not be able to change the absorbance at the isobestic point. As such, if for a particular buffer concentration and test solution, it could experimentally be ascertained that there was not much difference between the absorbancies of (indicator + buffer) and (indicator + buffer + wetting agent), then it may reasonably be assumed that there is not much micelle formation and that the turbidity effect is negligible. When a search for such conditions was made, it was experimentally found that a diluted buffer of the composition shown below gave the desired results:

Buffer composition : 1·1 c.c. of 1 N — Na Ac + 1·18 c.c. of 0·9868 N — HCl in 50 c.c. of test solution.

Test solutions made with the above buffer + indicator gave the same absorbance at a wavelength corresponding to isobestic point for thymol blue (482 $m\mu$) both in the absence and presence of WA (0·2%).

Accordingly, another set of experiments was carried out with above buffer and the apparent pH shifts thus computed and shown in Table I, Column 5 indicate a more regular behaviour. A diluted buffer such as this also avoids any complications due to the salt effect and high concentration of buffer.

It may be noted that in this case Δ pH gradually tends to become less negative as the concentration of the surface active agent decreases till finally at very low concentration of wetting agent (in the region of 0·05–0·02%) it becomes positive. It is worthwhile to note that none of the theories so far propounded are able to explain such behaviour and change in the sign of Δ pH.

Teepol.—A 1% (by volume) stock solution of teepol in water was prepared and was used as the stock solution. A buffer of pH 2·00 was employed. A 0·1% solution (by volume) of this detergent gives an apparent pH shift of 1·20. In view of the fact that its constitution and molecular weight could not be definitely ascertained, further work with this substance was not continued.

Dedocyl benzene sodium sulfonate.—A set of experiments with varying amounts of this detergent was carried out with buffers (made out of sodium acetate and hydrochloric acid) of different pH and ionic strengths. Unlike Manoxol-OT, this detergent is found to give quite clear test solutions and also the solubility is much higher. With the same experimental procedure, the absorbancies of standards and test solutions were measured. The apparent pH shifts were calculated and are presented in Table I, Columns 7 and 9.

It was observed in all the above cases that the apparent pH is always less than the Sorenson value and the pH shift increases continuously with increasing amounts of the wetting agent.

Discussion.—When an attempt is made to give a quantitative interpretation of these results on the lines of Krishnappa *et al.*, it is found that the respective values of K_1 and K_2 the stability constants, calculated from two different pairs of readings in the same set of experiments do not agree with each other (*see* Table II).

Further, the apparent pH calculated from the values of k_1 and k_2 (Table II) are quite different from the ones experimentally observed.

In the case of dodecyl benzene sodium sulfonate, the calculated value of k_1 comes out to be negative in all cases. So it appears that this surface active agent as well corresponds more to the case of Nekal BX[4] which did not follow the equation

$$-\Delta \text{ pH} = \log_{10} \frac{1 + k_2 C_w}{1 + k_1 C_w}$$

TABLE II

Surface active agent	pH of the test solution used (Sorenson value)	Values calculated from the equation $-\Delta\ pH=\log_{10}\frac{1+k_2 C_w}{1+k_1 C_w}$		Reference to Table I
		k_1	k_2	
Manoxol-OT ..	2·7	33·18	794·75	*Vide* items 3 and 4 of column 5
	2·7	52·08	1145·10	*Vide* items 1 and 2 of column 5
Dodecyl Benzene Sodium Sulfonate	3·0	− 83·24	10971·5	*Vide* items 5 and 6 of column 7
	2·3	−148·70	9052·0	*Vide* items 5 and 6 of column 9

than to the case of Igepon T which followed the equation. Further work, therefore, seems to be necessary to clarify the phenomenon and to give a more generally applicable quantitative treatment by taking into account some factors, most important of which appears to be micelle formation, which have perhaps so far been not fully considered.

ACKNOWLEDGEMENT

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THE ELECTRICAL CONDUCTIVITY OF SILICA SOLS

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The conductivity of silica sols has been investigated by a number of workers. Robinovitsch and Laskin[1] determined the H^+ concentration of silica sol and concluded that the adsorbed silicic acid is dissociated to a greater extent than in true solution. Ghosh and Dhar[2] observed that ageing of the silica sol is accompanied by an increase in conductivity. In the present investigation, negatively charged silica sols prepared by adding ammonia to purified silica gel are studied by measuring the change in conductivity on ageing as well as on dilution. Results obtained have been discussed to throw light on the nature of the stabilizing electrolyte.

Experimental

Several methods have been employed for the preparation of silica sols.[3] In the present investigation, negatively charged silica sols are obtained by the modification of the methods suggested by Farbenind[4] and Neundlinger.[5]

Sodium silicate solution (20%) was added to hydrochloric acid (3-N approx.) while constant stirring. The resulting mixture was subjected to continuous cold dialysis in a parchment paper bag till the gel was formed. The gel was then peptized with the required quantity of ammonia, the excess of which was removed by heating the sol on a water-bath at about 70° C. till free from ammonia. The sol so obtained was further purified by continuous cold dialysis for the required period. It was found that stable sols of fairly high concentration and purity can be prepared by this method.

Silica content of the sol was determined on evaporating to dryness 10 ml. of the sol in a previously weighed crucible at a temperature 110–20° C. To determine ammonium ion, an aliquot portion of the sol was coagulated, filtered and washed. Ammonia was estimated in the filtrate by treating it with an excess of standard NaOH solution, the excess after the reaction being estimated by titrating with standard HCl solution.[6] Chloride was found to be absent in all the samples. Table I gives composition of various sols.

TABLE I

Sol	Silica (g./l.) *a*	NH_4^+ ion concentration (g./l.) *b*	NH_4^+ ion concentration (m.e./l.)	Purity *a/b*
F	36·7	0·162	9·0	226
G	34·0	0·288	16·0	118
H	45·0	0·1224	6·8	368
I	43·8	0·0864	4·8	507
J	35·8	0·0648	3·6	552
K	43·4	0·1008	5·6	431

CHANGE IN CONDUCTIVITY ON AGEING

The conductivity of silica sol K was measured over a number of days. Double distilled water (sp. conductivity $= 2\times10^{-6}$ mhos. at 35° C.) was employed for dilution and its conductivity was neglected. Dilutions were checked by analysis. The conductivity of the sols was measured at 35° C. as shown before.[7] The data are represented graphically in Fig. 1.

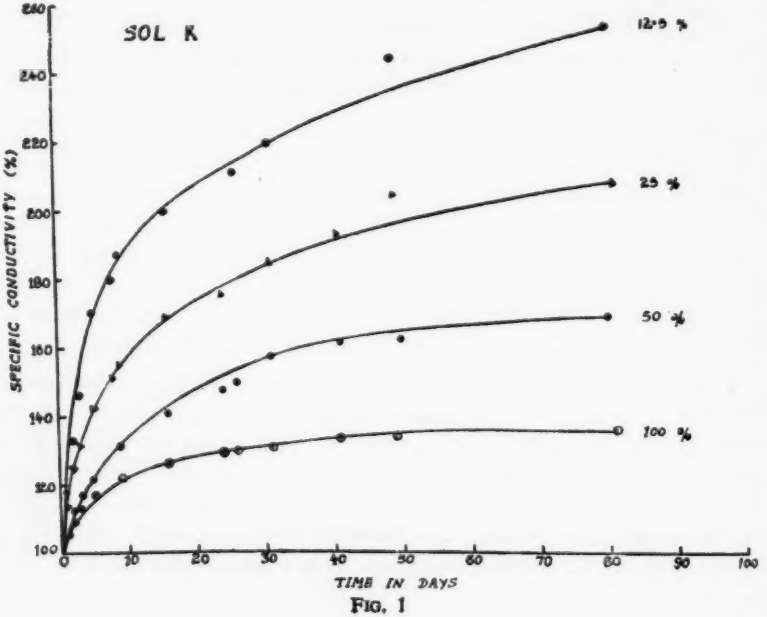

FIG. 1

Change in Conductivity on Dilution

Change in conductivity on dilution was followed in the case of sols, F, G, H, I and J. Table II gives the data regarding the sp. conductivity and eq. conductivity of the micelles in the case of sols I and J.

Table II

Sol	Concentration of the sol silica (g./l.)	Concentration of NH_4^+ ion in the micelles (m.e./l.)	Specific conductivity of the micelles $K \times 10^5$	Equivalent conductivity of the micelles
I	43·8	4·80	13·68	28·49
	39·42	4·32	12·20	28·24
	35·04	3·84	10·50	27·35
	30·66	3·36	9·815	29·21
	26·28	2·88	7·962	27·65
	21·90	2·40	7·252	30·21
	17·52	1·92	5·833	30·38
	13·14	1·44	4·794	33·29
	8·76	0·96	3·512	36·58
	4·38	0·48	2·335	48·65
J	35·8	3·60	7·042	19·64
	32·22	3·24	6·261	19·33
	28·64	2·88	5·624	19·53
	25·06	2·52	4·903	19·45
	21·48	2·16	4·196	19·42
	17·90	1·80	3·660	20·33
	14·32	1·44	2·995	20·80
	10·74	1·08	2·580	23·89
	7·16	0·72	1·973	27·40
	3·58	0·36	1·310	36·39

DISCUSSION

Effect on Ageing.—It is obvious that in all cases the specific conductivity of the sol increases on ageing, the rate of increase being greater, greater the dilution (*see* Fig. 1). The increase in conductivity on ageing of the silica sol has been observed previously by Ghosh and Dhar.[2] Sol K used in the present investigation was of a fairly high degree of purity and did not contain any chloride. Since the silica gel was peptized with ammonia, the sol so formed may be stabilized by either the OH ion or the SiO_3 ion with ammonium ion as the gegenion. In other words, the stabilizing electrolyte may be either ammonium hydroxide or ammonium silicate. When the sol is allowed to age, there is a perceptible increase in conductivity owing to the stabilizing electrolyte coming out of the surface of the colloidal particles into the intermicellar liquid. If we assume ammonium hydroxide to be the stabilizing electrolyte, the increase in conductivity on ageing cannot be explained, as ammonium hydroxide which may come out in the intermicellar liquid is a weak electrolyte. Alternatively, we may assume that ammonium silicate is the stabilizing electrolyte and the increase in conductivity is due to its coming out in the intermicellar liquid. However, ammonium silicate is a salt of very weak silicic acid ($K = 1{\cdot}6 \times 10^{-10}$)[8] and a weak base, ammonium hydroxide ($K = 1{\cdot}8 \times 10^{-5}$)[9]. Taking the ionic product of water $K_w = 10^{-14}$ and the concentration of ammonium silicate as $0{\cdot}02\,e$ per litre, the hydrolytic constant and the degree of hydrolysis can be easily calculated. The hydrolytic constant and the degree of hydrolysis comes out to be 3·5 and almost 100% respectively. Even sodium silicate is completely hydrolysed in 1/48 N solution.[10] Hence, it appears difficult to explain the increase in conductivity due to the deadsorption of ammonium silicate. The only explanation appears to be to assume that the hydrolysis of the electrolyte is inhibited as it is adsorbed on the colloidal particle. The state of equilibria may be represented as follows:—

$$\underset{\text{adsorbed}}{(NH_4)_2SiO_3} \rightleftharpoons \underset{\text{free}}{(NH_4)_2SiO_3} \rightleftharpoons \begin{array}{l} 2\,NH_4^+ + SiO_3^{--} \\ \Downarrow \qquad\quad H_2O \\ 2NH_4OH + H_2SiO_3 \end{array}$$

Thus, ammonium silicate may not be completely hydrolysed in the presence of adsorbed ammonium silicate. If the hydrolysis takes place completely, the equilibrium will be entirely shifted on the right hand side and the sol should become immediately unstable on dilution.

Effect on Dilution.—The sols F, G, H, I and J are of fairly high degree of purity and do not contain any free foreign electrolyte. In all cases, the specific

conductivity of the sol decreases with purity (*see* Fig. 2). This is in agreement with the observation of Chakravarti and Dhar,[11] Desai and co-workers[12] and Trivedi, Bhatt and Divatia.[13]

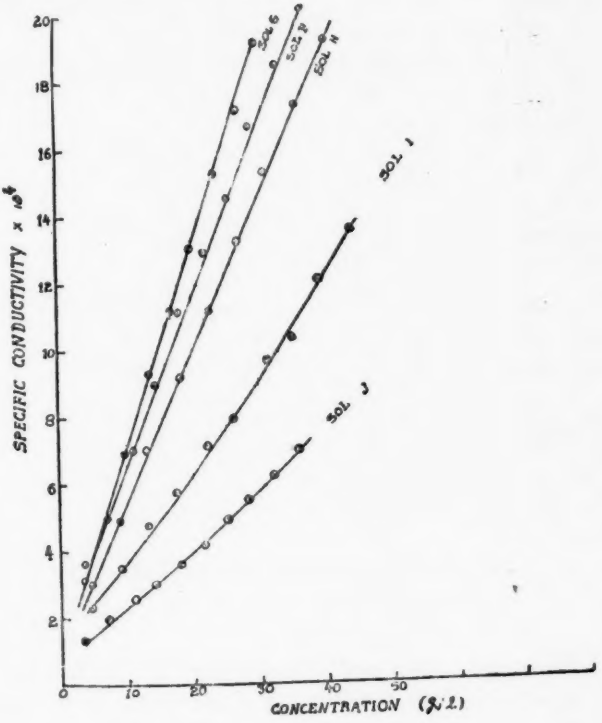

FIG. 2

Table II contains the equivalent conductivity of the micelles in the case of sols I and J. The equivalent conductivity of free ammonium silicate will be about 150 mhos approximately (calculated indirectly). Hence, the equivalent conductivity of the adsorbed ammonium silicate is a fraction of its value in the free condition. The behaviour of the sols F, G and H is also found similar (data not given). It may be further observed that in the case of sols I and J, the equivalent conductivity of the micelles decreases on dilution and then increases on further dilution. The data are graphically shown in the case of sol J (*see* Fig. 3).

The behaviour of silica sol is in harmony with that of sulphur sol,[14] iron oxide sol,[7] chromium oxide sol[13] and aluminium oxide sol.[15] The decrease

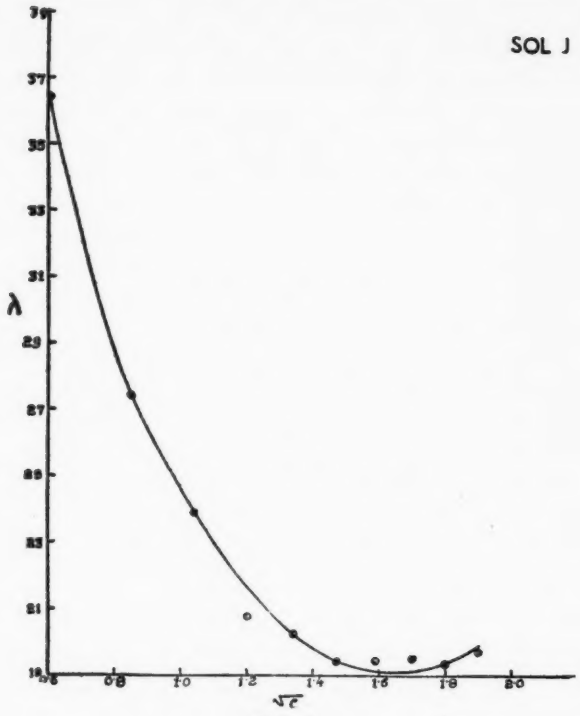

FIG. 3

in the equivalent conductivity on dilution followed by increase in conductivity on further dilution is similar to the behaviour shown by the soap solution. To that extent all the systems mentioned above may be classified as colloidal electrolytes. It may be remarked that the behaviour as a colloidal electrolyte becomes prominent only with sols of very high degree of purity.

SUMMARY

In the case of silica sols prepared by peptizing silica gel with ammonia, ammonium silicate is the stabilizing electrolyte. When the sols are allowed to age, the specific conductivity of the sol increases due to the deadsorption of ammonium silicate. Although ammonium silicate is a salt of a weak base and a very weak acid, it is not completely hydrolysed under the conditions of the experiments. The adsorbed ammonium silicate behaves as a colloidal electrolyte and its equivalent conductivity is a fraction of its value in the free condition.

ACKNOWLEDGEMENT

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THE NEAR ULTRAVIOLET EMISSION SPECTRUM OF TETRALIN (TETRAHYDRONAPHTHALENE)

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Abstract

An emission spectrum of tetralin (tetrahydronaphthalene) in the near ultraviolet excited by a transformer discharge through flowing vapour has been studied and about twenty-nine bands in emission have been photographed and measured on suitable instruments. Vibrational analysis of the bands in terms of the fundamental frequencies of the molecule is proposed and is compared with those obtained in the corresponding absorption spectrum of tetrahydronaphthalene studied by the author.[2] The results afford further confirmation of the correctness of the analysis and particularly the assignment of the (0, 0) band proposed in the absorption spectrum of the molecule.

Introduction

The ultraviolet absorption spectrum of tetralin in solution has been reported by Weinstock and Boekelheide.[5] Its absorption spectrum in the vapour state has been reported by the author.[2] So far no work on emission spectrum of tetralin appears to have been reported. The present work deals with its emission spectrum excited by an uncondensed transformer discharge through the flowing vapour of the substance. The ground state vibration frequencies of tetralin are known from its infra-red and Raman spectra.[4] It was observed that in vapour absorption the ground state frequencies could not be identified with those found in Raman and infra-red spectra and hence the work on emission spectrum was undertaken. These investigations explain some of the peculiarities observed in the spectrum of vapour absorption.

Tetralin can be considered essentially as an *o*-dialkyl substituted benzene since the nonplanar saturated six membered ring is not expected to make any profound difference in the spectrum. The emission spectrum is hence compared with the emission spectra of *o*-xylene[1] and *o*-cresol[3] obtained by other workers.

Experimental

The emission spectrum of tetralin was obtained by means of an uncondensed transformer discharge. The discharge tube was of pyrex glass and had the conventional π-form. It was about 80 cm. in length and about 1·5 cm. in diameter. One end of the discharge tube was sealed off while a quartz window was attached at the other end with sealing wax. As the sealing wax is attacked by the substance it was necessary to seal the quartz window repeatedly after about every six hours. The electrodes consist of hollow aluminium cylinders about 1 cm. in diameter and were about 75 cm. apart. Vertically below the electrodes, tubes of about 6 inches in length were sealed to the discharge tube to collect the liquid which is formed during the discharge. The discharge brings about a deposit of a dark reddish-brown thick liquid. The quartz window was about 3 cm. away from the nearest electrode. The substance to be investigated was contained in a side bulb attached to the discharge tube near the quartz window. The tube was evacuated by a Cenco hyvac pump which was connected suitably to the other end of the discharge tube. A trap immersed in ice was also included between the discharge tube and the pump to reduce the amount of the substance escaping to the pump. The pump was kept continuously running during the period of exposure. The excitation source consisted of a variac and a 0·25 Kilowatt Hilger transformer. The discharge was maintained throughout the present investigations by applying the minimum voltage necessary. This was found to be about 2,000 volts under the continuous flow of vapour when a faint greenish glow could be seen in the discharge. Under higher voltage the discharge glow becomes brighter and there is decomposition of the substance. The emission spectrum was recorded on a Hilger medium quartz spectrograph, the exposure time needed being about 72 hours.

Results

The spectrum consists of twenty-nine fairly sharp bands in the region 2695–2895 Å, superposed by a continuum beginning at about 2700 Å and extending to beyond 2900 Å (Fig. 2). All the spectra taken were centrally superposed by the spectrum of an iron arc taking about two amperes on 220 volts D.C. This served as a source of standard lines for measuring the plates. Plates were measured on a Hilger Comparator whose least count is 0·0001 cm. Three plates were measured and the mean of the three wavelengths was taken and converted to wave numbers in vacuo using Kayser's tables. The values are correct to about $\pm$ 4 cm.$^{-1}$ in the case of strong bands and about $\pm$ 8 cm.$^{-1}$ in the case of weak bands. The results are recorded

in Table I. In Fig. 1, the emission spectrum obtained with present investigation and the vapour absorption spectrum obtained at room temperature with a 2 meter column are shown. The corresponding bands have been made to coincide.

TABLE I

Near ultraviolet emission bands of tetralin (tetrahydronaphthalene)

(Intensity visual estimation in terms of 10)

λ in A in air	ν cm.$^{-1}$ in vacuo	Intensity (visual)	Separation from (0, 0), *i.e.*, from 36791 cm.$^{-1}$	Assignment
2695·2	37092	1	301	0+301
2699·9	37027	0	236	0+236
2703·5	36978	0	187	0+187
2708·0	36916	0	125	0+125
2711·1	36874	2	83	0+92
2714·3	36831	1	40	0+45
2717·2	36791	5	0	(0, 0)
2721·0	36740	1	51	0−51
2724·2	36697	1	− 94	0−94
2728·7	36636	1	−155	0−155
2731·9	36593	0	−198	0−198
2744·0	36432	0	−359	0−359
2753·3	36309	1	−482	
2762·5	36188	0	−603	
2765·9	36143	00	−648	
2772·0	36064	10	−727	0−727
2776·3	36008	1	−783	0−727−51
2779·4	35968	00	−823	0−727−94
2783·6	35914	00	−877	0−727−155
2796·5	35748	8	−1043	0−1043
2800·4	35698	1	−1093	0−1043−51
2803·7	35656	0	−1135	0−1043−94
2809·2	35586	7	−1205	0−1205
2816·7	35492	0	−1299	0−1205−94
2821·2	35435	0	−1356	0−1205−155
2854·2	35025	2	−1766	0−1043−727
2866·8	34871	2	−1920	0−1205−727
2880·4	34707	2	−2084	0−1043−1043
2893·7	34547	2	−2244	0−1043−1205

Discussion

Tetralin can be essentially considered as an *o*-dialkyl substituted benzene since even though the two ortho-positions are bridged by a nonplanar saturated six-membered ring the latter is not expected to disturb the electronic spectrum profoundly. The near ultraviolet vapour absorption spectrum reported earlier demonstrates the validity of such a deduction. In fact it is shown that the absorption spectrum shows a great similarity not only with *o*-xylene but also with other *o*-disubstituted benzenes as far as the vibrational structure of the spectrum is concerned. It was however observed that the bands involving ground state frequencies specially those on the longer wavelength side of the 0–0 band did not give the correct frequency intervals as found in Raman and infra-red spectra. This was attributed to an impurity of naphthalene in the sample of tetralin. This however, left the assignment of the 0–0 band rather tentative as also the molecular species responsible for absorption.

The near ultraviolet emission spectrum of tetralin starts with a fairly strong band at 36791 cm.$^{-1}$ This coincides with the strongest band in absorption at 36790 cm.$^{-1}$ which is taken as the 0–0 band. Figure 1 also shows that all the bands in this group are common to emission and absorption. The emission spectrum also shows a band on shorter wavelength side of the 36791 cm.$^{-1}$ band which has a corresponding band in absorption. This shows that the emission spectrum obtained corresponds to the absorption spectrum reported. Thus the band at 36791 cm.$^{-1}$ in emission is taken as the 0–0 band in common with absorption. The medium intensity of this band in emission as compared to some of the stronger bands on the longer wavelength can be understood as due to self-absorption. The vibrational analysis further confirms the choice of the 0–0 band as would be seen presently. Thus the emission spectrum confirms unambiguously the choice of the 0–0 band.

The most intense bands on the longer wavelength side of the 0–0 band at 36064, 35748 and 35586 cm.$^{-1}$ are separated from the 0–0 band by 727, 1043 and 1205 cm.$^{-1}$ Comparison of the data from Raman spectrum shows that these frequency intervals correspond to the frequencies of three intense Raman lines and hence represent ground state fundamentals possibly of the totally symmetric type. The bands corresponding to these ground state frequencies however are not observed in the absorption spectrum as has already been mentioned. This was explained as being probably due to the impurity of naphthalene found in the sample of tetralin employed. In the emission spectrum there are bands involving combinations of these frequencies and a few overtones. The frequencies principally involved

in the emission spectrum of tetralin and other two *o*-disubstituted benzenes which have been investigated are compared in Table II. It is observed that there is a close correspondence between the spectra. The corresponding frequencies involved in the spectra of these three compounds can be possibly correlated to the similar frequencies of the parent compound namely benzene. The above analogy thus shows that the emitter in the present case is the tetralin molecule. This also lends support to the view that the difficulty of observing ground state frequencies in absorption due to naphthalene impurity arises out of some type of interaction between these molecules.

The emission spectrum thus shows the excitation of three ground state frequencies namely 727, 1043 and 1205. The absorption spectrum principally involved the excited state frequencies 682, 951 and 1185 cm.$^{-1}$ and hence these are correlated to the ground state frequencies as shown in Table III in the previous work.[2] Apart from these, there may be a still smaller frequency analogous to 260 cm.$^{-1}$ in *o*-xylene or 278 and 192 cm.$^{-1}$ of *o*-Cresol. But since the combinations of these frequencies with other frequencies are not observed it is not possible to assign them unambiguously. The Raman and Infra-red data are rather insufficient in this range and only record a frequency 263 in Raman effect. The emission spectrum however does not show any ground state frequency of that order.

It is significant to find that some of the split components corresponding to 606 e_g^+ frequency of benzene is involved in emission. In *o*-Cresol emission the 524 cm.$^{-1}$ gives a strong band and there is also the corresponding band in *o*-xylene emission. In the emission of tetralin there are weak bands separated from 0–0 band at 482, 603 and 648 cm.$^{-1}$ but none of these corresponds to Raman frequencies. They do not also give any combination band with other strong frequencies. This seems to be a unique case where none of the components corresponding to 606 e_g^+ frequency of benzene is excited. There are bands separated from strong bands involving the ground state frequencies 51 and 94 cm.$^{-1}$ on the longer wavelength side. These small frequencies are classified as due to v–v transitions. The values corresponding to these in absorption were found to be 46 and 86. It is found that the difference between the ground state frequency of 727 cm.$^{-1}$ and its excited state frequency of 682 cm.$^{-1}$ is 45 and the corresponding difference between 1043 and 951 is 92. But it is unlikely that such high frequencies are involved in v–v transitions. The coincidence may be purely accidental.

TABLE II

Ortho-cresol			Ortho-xylene			Tetralin		
Ground state frequencies		Excited state frequencies	Ground state frequencies		Excited state frequencies	Ground state frequencies		Excited state frequencies
Raman	U.V. emission	U.V. absorption	Raman	U.V. emission	U.V. absorption	Raman	U.V. emission	U.V. absorption
190	192	124	256	260				
274	278	202						
526	524	360	505	505	375			
584	590		582	580	505			
748	744	702 719	733	733	692	725	727	682
1044	1040	944	1052	1054	940	1039	1043	951
1154	1163	955						
1254	1261	1251	1223	1230	1195	1203	1205	1185
			1380	1365				
			1584	1600				

All frequencies are expressed as wavenumbers ($cm.^{-1}$).

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SUMMARY

The near Ultraviolet emission spectrum is studied in the present investigation. The spectrum consists of sharp bands. Vibrational frequencies in the ground state have values 727, 1043 and 1205 cm.$^{-1}$ and combinations and overtones of these are found to be present as discussed and mentioned in the analysis. These frequencies have been correlated with the Raman frequencies and the infra-red frequencies of the molecule. The frequencies in the emission spectra of *o*-xylene and *o*-cresol are compared with those of tetralin and similarity between them is pointed out. The results confirm the correctness of the assignment of the (0, 0) band in the absorption spectrum of tetralin.

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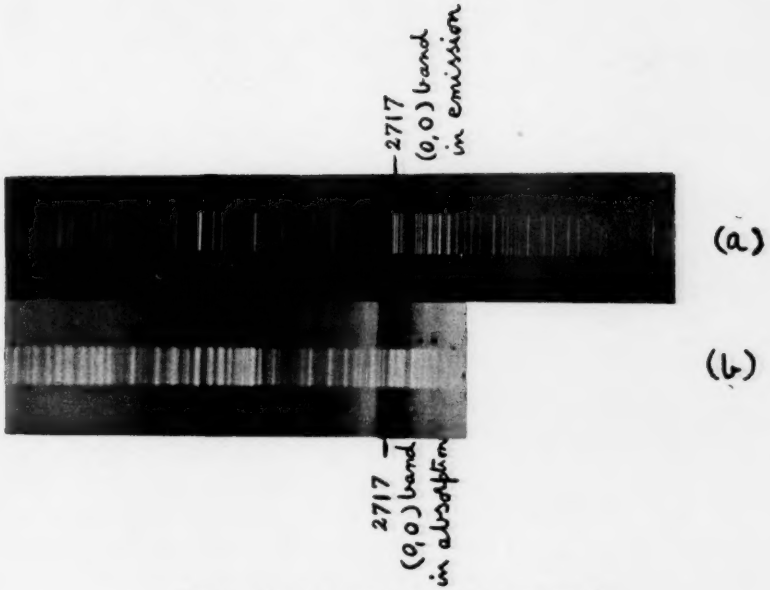

FIG. 1. (*a*) (0, 0) band in emission at 2717 Å.
(*b*) (0, 0) band in absorption at 2717 Å in Tetralin.

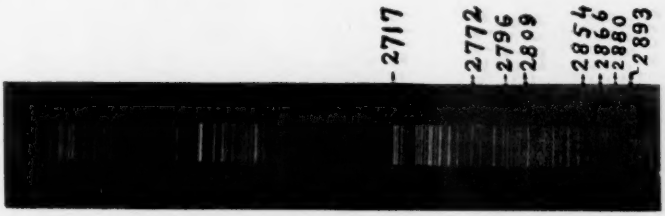

FIG. 2. Emission spectrum of Tetralin.

ORE-MICROSCOPIC STUDIES OF THE MANGANESE ORE-MINERALS OF OLD M.P.

I. Dongribuzurg, Bhandara District

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Received September 16, 1958

(Communicated by Prof. Sripadrao Kilpady, F.A.SC.)

INTRODUCTION

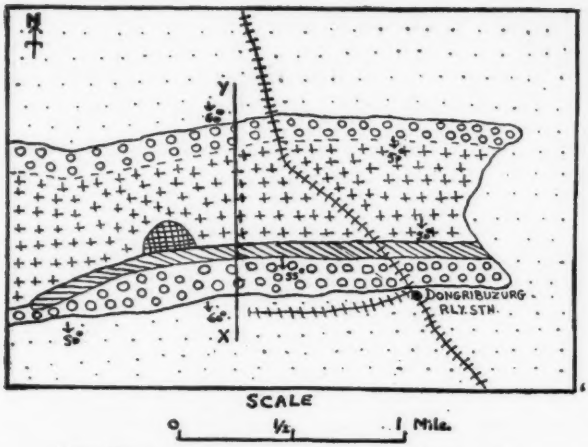
AN attempt is made here to give a systematic account of the ore-microscopic studies of the manganese ore-minerals collected from the Dongribuzurg manganese mine of the C.P.M.O. Co., in Bhandara District. The area forms a part of the topographical sheet No. 55–0/10 and is situated about a furlong west of the Dongribuzurg railway station, which is nearly 14 miles north of the Tumsar railway station on the Tumsar Road-Tirodi branch of the South Eastern Railway. The deposit consists almost entirely of secondary manganese minerals like Pyrolusite and Psilomelane associated with highly metamorphosed rocks like Gondite (Spessartite-Quartz rock), Sillimanite-Garnet-schist and Gneisses. It is interesting to note here that other deposits, on the same line of strike and situated about 2–3 miles away, consist of manganese ore-minerals of medium to high grade regional metamorphism like Bixbyite, Hollandite and Braunite.

GEOLOGY OF THE AREA

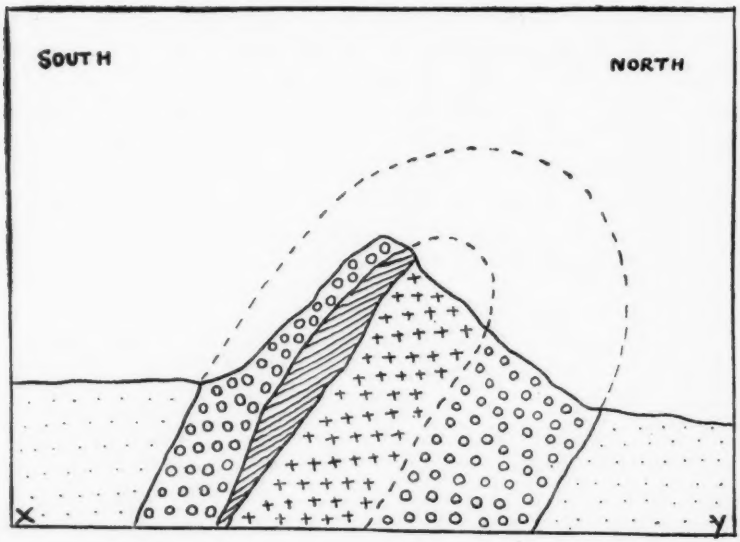
The deposit forms a ridge running approximately east-west and is about 1½ miles long. The ore-band forms a consistent horizon running WSW-ENE except at the west end where the strike changes to E-W. It has a dip of about 50°–60° south. The foot-wall consists of coarse-grained muscovite schist with garnet and sillimanite and with numerous veins of quartz running parallel to the strike. The hanging wall is a felspathic mica schist while further south, a medium-grained biotite gneiss overlies it. The rocks belong to the Sausar series of the Dharwars. A granitic intrusion is present near the ore-body in the western portion. The geological map of the area and a structural section is given (Text-Figs. 1 and 2).

NATURE OF THE ORES

The ores are predominantly a mixture of Psilomelane and Pyrolusite occurring partly in botryoidal, stalactitic, mammillary and concretionary



TEXT-FIG. 1. Geological Map of Dongribuzurg Area.



TEXT-FIG. 2. An Approximate Structural Section (along XY in the Map) showing an Isoclinal Fold

SUCCESSION

- Granite
- Muscovite-Biotite Schistose Gneiss
- Felspathic Schist and Quartzite with Vein Quartz
- Gondite and Manganese Ore
- Coarse Muscovite Schist with Garnet and Staurolite

forms. At places the ore is compact and crystalline and associated with some hematite. Braunite, the typical ore-mineral usually associated with gondites, is also found as a subsidiary associate with Pyrolusite and Psilomelane.

A detailed study of a number of polished sections prepared from carefully selected samples has revealed the following ore-minerals: (1) Psilomelane, (2) Pyrolusite and Polianite, (3) An unidentified new (?) mineral, (4) Braunite, (5) Hematite. The reflectivity values in air were determined by the help of the Berek's Slit-microphotometer using green light.

A descriptive account of the ore-minerals is given below.

Psilomelane

This appears to be the most important constituent of the ores along with Pyrolusite. It occurs in a variety of forms—botryoidal, stalactitic, mamillary, in the form of concentric layers alternating with those of Pyrolusite and rounded lumps, all suggesting deposition from a colloidal state, and as veinlets replacing Braunite. At one place, a fibrous variety of Psilomelane is found veining ordinary Psilomelane (Plate VII, Fig. 6). It is quite coarse-grained and clearly exhibits pleochroism and high anisotropism with grey, yellowish, bluish grey and white colours and undulatory extinction. The reflectivity value (28·5) is higher than that of Psilomelane. The characteristics of this fibrous vein mineral recalls the description of Romanéchite. According to Uytenbogaardt (1951), some of the material found at Romanéche, France, is Psilomelane while some is Cryptomelane. The identity of the mineral can only be established after an X-ray diffraction analysis, which will be undertaken later on.

The properties of Psilomelane are as follows:—

It takes a good polish. Colour: Grey to bluish grey. Reflectivity: Moderate, the value for green light varying from 27 to 30 (usually 28). Pleochroism: Distinct in shades of grey and bluish grey under high power. Anisotropism: Strong. It cannot be observed easily due to the very fine-grained nature but under high power, the mineral seems to be composed of highly anisotropic needles showing straight extinction.

The mineral is usually found in aggregates of extremely fine needles. It also forms botryoidal masses consisting of concentric alternating layers of Pyrolusite, intimate mixture of Pyrolusite and Psilomelane and pure Psilomelane. It alters to Pyrolusite and every stage in this alteration is met with. Shrinkage cracks in these concentric layers are filled up with fine-grained

Pyrolusite (Plate VII, Fig. 1). Psilomelane also veins and replaces Pyrolusite in a Pyrolusite-Braunite ore.

Etch reactions

Positive.—HNO_3—Stains light brown or negative. Fumes tarnish. HCl—Permanently tarnishes light brown. Fumes tarnish. $FeCl_3$—Light grey stain. H_2O_2—Effervescence. Surface unaffected. $SnCl_2$ (saturated) + HCl (concentrated)—Stains black. Effect less on coarse fibrous variety. H_2O_2 (concentrated) + H_2SO_4 (concentrated)—Stains completely black. Effect stronger on fine-grained aggregates.

Negative.—KCN, KOH, $HgCl_2$, H_2SO_4 (concentrated), Aqua regia.

Pyrolusite

This mineral is nearly as abundant as Psilomelane. It does not take a good polish because of its inferior hardness. Colour: White with a distinct yellow tint in oil. Reflectivity: High, the value in green light varies from 30–34 for fine-grained aggregates and from 34–39 for coarse crystals. Pleochroism: Distinct. Greyish white to yellowish white. Anisotropism: Strong. Yellowish, yellow-brown, greenish blue and grey colours. Extinction is straight with four distinct extinctions per revolution. Prismatic (one direction) cleavage is distinct especially in bigger crystals.

The mineral occurs as fine to very fine-grained aggregates of prismatic needles which are sometimes radiating and sometimes fibrous (Plate VII, Fig. 5). Coarse prismatic needles occur interpenetrating each other or in parallel bands, the orientation of the needles between two adjacent bands being different (Plate VII, Fig. 2). Layers of prismatic needles are also found in concentric layers of Psilomelane. In these layers, the needles are usually radiating and are arranged at right angles to the concentric layers. Pyrolusite in the outer layers is more coarse-grained than that found in the inner layers. Shrinkage cracks in Psilomelane are filled with medium to fine-grained Pyrolusite and the latter also irregularly veins the Psilomelane (Plate VII, Fig. 1). Fine-grained Pyrolusite is often found intimately intergrown with coarse-grained Hematite, which it veins and replaces along with Psilomelane. Coarse-grained Pyrolusite also occurs with coarse-grained Hematite. This Pyrolusite (Polianite) may perhaps be regarded as the first generation Pyrolusite crystallising along with Hematite, in order to distinguish it from that formed by the crystallisation of the colloidal Psilomelane. Interlocking crystals of medium-grained Pyrolusite and Braunite have been noticed in one section (Plate VII, Fig. 4). This Pyrolusite also is probably to be regarded as of first generation.

Etch reactions

Positive.—HNO_3—Stains light brown on very fine-grained specimens probably mixed with Psilomelane. Otherwise negative. HCl—Stains some specimens brown. H_2SO_4 (concentrated)—Permanently tarnishes some specimens. $FeCl_3$ (saturated)—Tarnishes some specimens grey-brown. $SnCl_2$ (saturated) + HCl (concentrated)—Blackens instantaneously. H_2O_2—Vigorous effervescence. Tarnishes some coarse-grained specimens. H_2SO_4 (concentrated) + H_2O_2 (concentrated)—Stains completely black.

Negative.—HNO_3, HCl, KCN, KOH, $HgCl_2$.

An Unidentified New (?) Mineral

This mineral occurs along with Pyrolusite, Psilomelane and Hematite. Its properties do not correspond to those of any known manganese mineral.

It takes a fairly good polish. Colour: Grey to dark brownish grey. Reflectivity: Very low. The value cannot be determined accurately because of its fine-grained nature and rarity of occurrence, but it is distinctly lower than that of Sphalerite and is about 14–15. Pleochroism: Clearly distinct in shades of grey and brownish grey. Anisotropism: Very high but without any typical colours. Yellowish or white. Extinction is undulose and patchy because of radiating texture. No internal reflections are visible even in oil.

It occurs as aggregates of small grains, each grain containing crystals with radiating texture. It is sometimes associated with Psilomelane and in one section it probably forms a vein along with it (Plate VII, Fig. 3).

Etch Reactions

Positive.—$SnCl_2$ (saturated) + HCl (concentrated)—Faintly tarnishes brownish.

Negative.—HCl (concentrated), H_2SO_4 (concentrated) + H_2O_2 (concentrated).

This mineral exhibits properties resembling those of Hausmannite, Manganite and Hetaerolite but differs from them in not showing red internal reflections and in being negative to almost all important etch reagents. X-ray diffraction studies to be shortly undertaken may reveal the identity of the mineral.

Braunite

This mineral is present in subordinate quantities associated with Pyrolusite and Psilomelane.

It takes a good polish. Colour: Grey with a faint brownish tint. Reflectivity: Low. The value varying from 18·5–19·5. Pleochroism: Very weak. Anisotropism: Weak but distinct. Grey and brown colours.

It forms medium to fine-grained granular masses and interlocking crystals with medium-grained Pyrolusite. Both these minerals are excessively veined and replaced by Psilomelane (Plate VII, Fig. 4).

Etch Reactions

Positive.—H_2O_2—Slow effervescence. No stain. $H_2O_2+H_2SO_4$ (concentrated)—Faster effervescence. Darkens and produces etch scratches. After 4 minutes develops parting planes. $SnCl_2$ (saturated) + HCl (concentrated)—Tarnishes permanently brown and develops etch scratches. After 4 minutes strong action.

Negative.—HNO_3, HCl, KCN, $FeCl_3$, KOH, $HgCl_2$, Aqua regia.

TEXTURAL FEATURES

The characteristic feature of the ores is the colloform texture exhibited by Psilomelane. Concentric bands, composed of Psilomelane, Pyrolusite and their intimate mixtures, alternate. This suggests a gel origin. Edwards (1947) remarks that "Where the original gel has crystallised, it results in the formation of radially arranged columnar crystals, whose long axes are normal to the outer (free) surface of the layer. A free surface, if present, is typically smooth, commonly with a high gloss or lustre, corresponding to the smooth 'skin' of a gel, and is distinct from the rough surface resulting from the co-termination of a growth of radially arranged crystals ....". Both these points are very clearly exhibited by the minerals. Pyrolusite, which crystallises after the dehydration of the gel, occurs as radiating columnar crystals whose long axes are normal to the free surface or the concentric rings. Moreover, the gel origin is supported by the cryptocrystalline character of Psilomelane and the shrinkage cracks in it which are perpendicular to the concentric lines and are filled with secondary Pyrolusite. The shrinkage cracks are obviously formed at the time of the dehydration of the gel.

Fine-grained Pyrolusite veins and replaces coarse-grained Hematite and remnants of Hematite with similar optic orientation are found scattered in a matrix of Pyrolusite. It also forms coarse-grained aggregates along with coarse-grained Hematite.

Medium-grained Braunite and Pyrolusite form interlocking crystals suggesting contemporaneous crystallisation. Both are excessively veined and replaced by Psilomelane.

Paragenesis

It is rather difficult to arrive at any definite conclusion about the paragenesis because the various minerals found in the area do not occur in one section (probably because they belong to slightly different suites) and hence their relationships are not very clear.

It is obvious that Braunite and Hematite are the first formed minerals. Some of the Pyrolusite which forms interlocking crystals with both Braunite and Hematite seems to have been formed contemporaneously. Braunite is veined and replaced by Psilomelane, and Hematite has been replaced by fine-grained second generation Pyrolusite and Psilomelane. Psilomelane exhibiting colloform texture has probably been formed after the solution and redeposition of the earlier formed metamorphic manganese minerals and probably also the first formed minerals like Braunite and Pyrolusite in the present association. Pyrolusite veins and replaces Psilomelane and is evidently secondary after it. The relation of Pyrolusite and Psilomelane with the unidentified mineral is obscure. But at one place it looks like a vein mineral along with Psilomelane. Its smaller grain size and fibrous nature also support this conclusion.

The probable sequence of formation appears to be as follows: Braunite, Hematite and Pyrolusite; colloform Psilomelane; Pyrolusite, the unidentified new (?) mineral and Psilomelane.

Origin of Pyrolusite

The occurrence of large quantities of Pyrolusite and Psilomelane with subordinate amounts of Braunite, associated with high grade metamorphic rocks like Gondite and Garnetiferous mica-sillimanite schist, is very interesting (Text-Fig. 1). Pyrolusite and Psilomelane are definitely epi-zone minerals. Their textures—mamillary, stalactitic, colloform—clearly indicate deposition from colloidal solutions. The structure of the area, perhaps, can offer a possible clue. The ore-band and the associated rocks form the crest of a compact isoclinal fold (Text-Fig. 2). It is known that the crests of folds in general and especially those of isoclinal folds are very unstable structures and are also more vulnerable to denudation. This weakness can produce a lot of cracks which can act as channels for subsurface waters which (charged with reagents like Carbon dioxide and the alkalies) might have dissolved and redeposited the ores to form Pyrolusite and Psilomelane. This process could have continued for a long time—even before the area was exposed to the surface by denudation—and could have completely changed the original nature of the minerals. The Sitasaongi and Chikhla ore-bands,

about 3–4 miles to the east, and which more or less form a continuation of the Dongribuzurg band, have an overturned sequence and form troughs of more gentle folds. These areas contain manganese ore-minerals like Sitaparite, Hollandite and Braunite which are characteristic minerals of medium to high grade regional metamorphism. This fact supports the view that the original deposit at Dongribuzurg might have consisted of high grade metamorphic ores which subsequently gave rise to Psilomelane and Pyrolusite after solution and redeposition.

SUMMARY

The paper gives an account of the ore-microscopic study of the manganese ore-minerals collected from Dongribuzurg, Bhandara District, Old M.P. The following are the ore-minerals that have been identified in polished sections: Psilomelane, Pyrolusite, Polianite and Braunite. The characters of these ore-minerals under reflected light are given along with their etch reactions and reflectivity values. In addition, a mineral showing properties different from those shown by any known manganese ore-mineral has been described. The identity of this mineral could only be established on chemical and X-ray studies which are now in progress. Interesting microstructures, like the colloform texture shown by Psilomelane, have been fully described, and the mineral paragenesis based on textural features is given. A note has been added on the origin of Pyrolusite, since the occurrence of large quantities of this mineral in association with highly metamorphosed rocks is curious and interesting.

ACKNOWLEDGEMENTS

The author is greatly indebted to Professor Sripadrao Kilpady, Head of the Department of Geology, Nagpur University, for his kind guidance and valuable suggestions. The author is also indebted to the Government of India, Ministry of Education, for the award of a Senior Research Training Scholarship.

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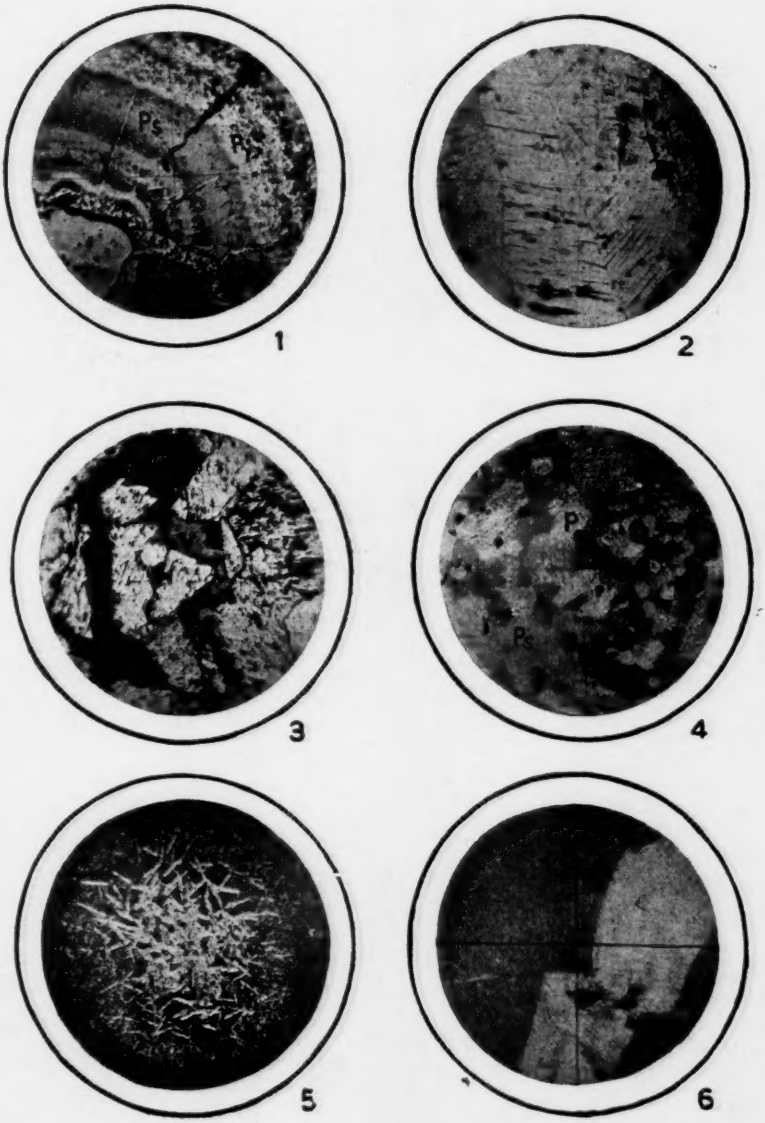

FIGS. 1–6

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Explanation of Plate VII

Fig. 1. Colloform texture exhibited by Psilomelane (Ps, grey). Pyrolusite (Py, white) fills the shrinkage cracks in Psilomelane and also veins it, ×60.

Fig. 2. Coarse-grained Polianite showing prismatic cleavage, ×60.

Fig. 3. A vein of the unidentified mineral (dark grey, V, in the centre) traversing Polianite (white), ×60.

Fig. 4. Braunite (B, dark grey) forming interlocking crystals with Polianite (P, white). Psilomelane (Ps, grey) replaces and veins both these minerals, ×60.

Fig. 5. Swarm of Pyrolusite needles (white) in Psilomelane (grey). Etched with HCl, ×60.

Fig. 6. Fibrous Psilomelane (white, showing strong anisotropism) veining ordinary Psilomelane (greyish black). Crossed Nicols, ×140.

KINETIC STUDIES IN ESTER HYDROLYSIS

Part IX. The Hydrolysis of Ethyl Acetate in Dioxan-Water Systems

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Introduction

In the previous Part (VIII) we reported the abnormalities in acid hydrolysis of ethyl acetate in water to which small additions of acetone were made. The present report deals with similar studies in which the organic solvent added is dioxan. Here too, it was observed in Part IV[2a] that small additions of organic solvent might not conform to the expected correlation for an ion-dipole reaction. Differences from the acetone-water system should, however, be expected for two reasons. The changes in dielectric constant for small additions of dioxan may not be appreciable as the change in water content is only of the order of 3 moles per cent. Unlike acetone, dioxan can provide two centres for the association of the proton but the hydrogen bond is weaker in the ether oxygen. If the dielectric constant is to exert a dominant influence, while a drift in the Arrhenius activation energy was anticipated earlier, this drift may not be large and the individual value may be expected to be close enough almost within the limits of experimental error. This drift may be even eliminated if by suitable addition of a neutral salt, dielectric constant changes are reduced still further.

Discussion of Results

The experimental results obtained are presented in Tables I and II while typical runs are given in the experimental part.

If one were to take only individual values and compare them, as anticipated, activation energy values are confined to a narrow range. The difference between the extreme values of 0·8 kilocalories, however, is outside the range of experimental error. Reckoning by standard statistical procedures for errors arising from temperature variations, analytical accuracy and errors in the measurement of time, values may be considered accurate to within 250 calories. The pronounced trend with a maximum value for the addition of about 6% by volume of dioxan (1·2 moles %) is clearly noticed in Fig. 1.

TABLE I

Rate constants and Arrhenius Parameters for the reaction

Dioxan in mixture		k_2 values at temperatures $\times 10$			E	$Log_{10}PZ$
% By volume	Mole fraction	30° C.	35° C.	40° C.	K. Cals.	
0	0	1·617 1·620*	1·862	2·817 2·812*	10·53	6·69
2	0·004288	1·649	1·929	2·882	10·60	6·80
4	0·008712	1·682	1·968	2·944	10·62	6·83
6	0·01347	1·699	2·009	3·030	10·97	7·09
8	0·01834	1·735	2·013	3·079	10·88	7·03
10	0·02344	1·671	1·961	2·851	10·14	6·49
10*	..	1·667*	..	2·845*	..	..

* Values taken from Part IV for comparison. All values of rate constants are in moles/litre, seconds^{-1}.

TABLE II

Rate constants in dioxan-water mixtures in the presence of 0·0444 M potassium acetate

% Dioxan by volume	k_2 values at temperatures			E K. Cals.	$Log_{10}PZ$
	30° C.	35° C.	40° C.		
0	0·1642	0·2142	0·2914	10·92	7·04
2	0·1668	0·2281	0·2986	11·07	7·13
4	0·1746	0·2341	0·3132	11·10	7·20
6	0·1682	0·2281	0·3016	11·10	7·18
8	0·1666	0·2158	0·2969	10·96	7·08
10	0·1652	0·2027	0·2849	10·34	6·62

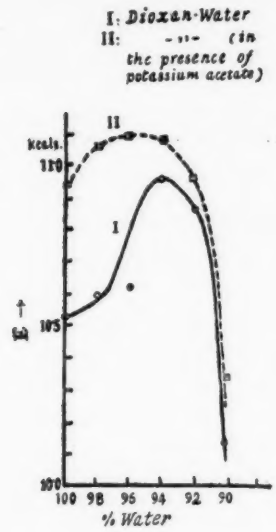

FIG. 1

The Fairclough-Hinshelwood correlation between the two Arrhenius parameters is also maintained in this region as may be seen from Fig. 2.

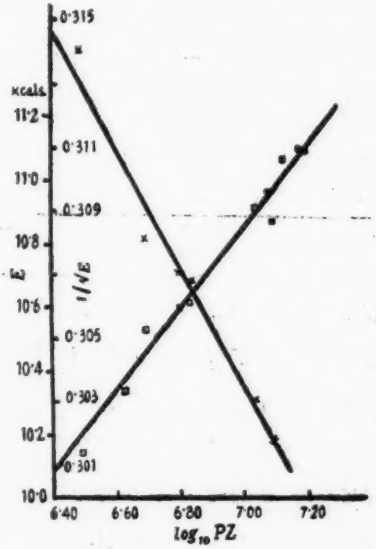

FIG. 2

The deviation from the normal dielectric constant-activation energy expected from the Kirkwood relationship[5] which appeared probable in the earlier part is thus confirmed in this solvent mixture also. The immediate effect of adding dioxan is presumably a disturbance of the quasicrystalline tetrahedral distribution of the water molecules which participate in the second stage of the reaction. Since the reactant in the first stage is also the solvated hydroxyl ion, the intervention of the dioxan disturbs also the solvation shell expected for this ion; it has been noticed[1] that both hydrogen and hydroxyl ions are solvated in aqueous systems with a distribution of water molecules as in water itself. This alters both the entropy of activation and the energy of activation that is actually observed. The effect of the dielectric constant of the environment becomes pronounced as the molefraction of water is reduced and the later additions of dioxan correspond to such correlation as reported in the earlier work.

Unequivocal evidence for neutral salt action in ester is not available.[3] The addition of an acetate to the system introduces the minimum of disturbance of the environment with acetanion as a product of the reaction. When present in quantities of the same order as the reactants but somewhat larger, in the initial stages, no change in the ionic strength may be expected and the principal effect is the one caused by a change in the dielectric constant of the medium. The influence of this changed environment is noticed in the results presented in Table II. The drift in the absence of added acetate is eliminated and the Arrhenius activation energy as well as the frequency factor becomes constant in the experimental region within the limits of experimental error. With increasing concentration of the organic solvent, addition of an acetate appears to be practically without effect as may be noticed in the system containing 10% by volume of dioxan (2·2 moles %). For a complete analysis of the position, values of activities of the reacting ions are necessary and are at present lacking. The need for this is clearly shown by the trend in the rate constant values presented in the table with an apparent maximum at 4% by volume of dioxan with added acetate (as against the maximum at 6% by volume in its absence). Again extreme values differ by an amount beyond the limits of experimental error.

While both acetone-water systems and dioxan-water systems confirm the anticipated deviations, a comparison of the abnormal regions in the two systems brings out certain differences. Acetone addition leads to a reaction rate change which is less than dioxan addition even though the dielectric constant can be expected to be higher. At the higher temperature the rate constants tend to approach each other especially when one considers the molefraction of water (Fig. 3).

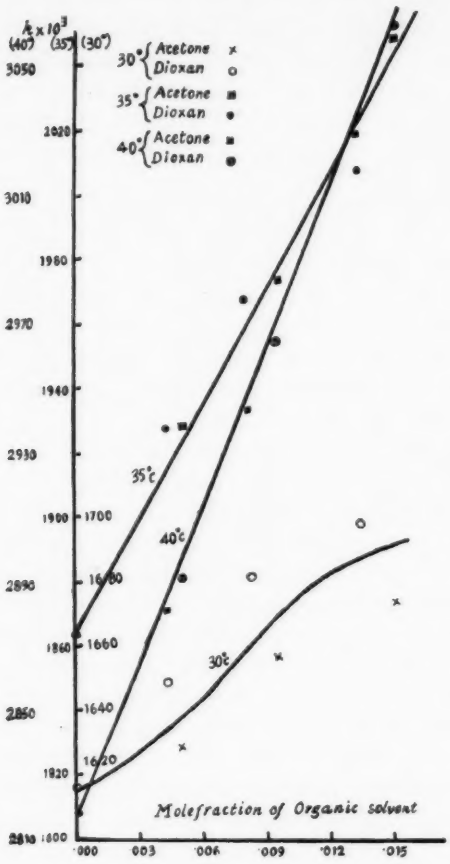

FIG. 3

The initial addition of dioxan or acetone alters the rate primarily by the disturbance of the quasicrystalline structure of the aqueous environment. This is clearly noticed in the increased values of entropy of activation in the initial stages as shown in Table III.

TABLE III

% Water by volume	100	98	96	94	92	90
Entropy of activation at 30° C. ..	26·07	26·44	26·89	26·89	26·66	25·24

TABLE IV

The alkaline hydrolysis at 30° C.

% Dioxan by Volume	Titre of 10 ml. HCl	Concentration			Titre value of aliquots				
		OH′	Ester						
0	19·50	0·02469 N	0·02584 M	Time in sec.	92·0	271·9	477·5	751·9	1440
				V_t	5·75	10·75	13·30	15·1	17·0
2	20·30	0·02529 N	0·024265 M	*t* sec.	82·45	260·0	445·6	656·6	914·5
				V_t	4·05	7·75	12·45	14·20	15·50
4	17·60	0·02595 N	0·02587 M	*t* sec.	110·0	288·8	497·3	815·2	1132
				V_t	3·90	8·75	11·25	13·20	14·20
6	19·10	0·02595 N	0·02321 M	*t* sec.	116·4	220·1	387·6	606·4	816·3
				V_t	4·10	7·25	10·15	12·05	13·20
8	19·20	0·02557 N	0·02760 M	*t* sec.	115·1	319·0	484·7	719·1	1018
				V_t	5·60	11·00	12·85	14·85	16·10
10	19·30	0·02615 N	0·02625 M	*t* sec.	140·5	331·8	511·3	913·2	1153
				V_t	5·70	10·40	12·50	14·85	15·60

TABLE V

The hydrolysis of ethyl acetate by hydroxyl ions at 35° C.

% Dioxan by Volume	Titre of 10 ml. HCl	Strength NaOH (moles)	Strength Ester (moles)		Titre value of aliquots				
0	18·80	0·02634	0·01981	t sec.	128·5	398·4	711·2	1010	1372
				V_t	3·60	8·70	10·85	11·90	12·50
2	18·70	0·02665	0·02284	t sec.	94·5	358·9	593·4	891·9	1272
				V_t	3·00	9·5	11·65	13·05	13·95
4	18·65	0·02704	0·02105	t sec.	95·2	192·4	681·9	809·8	1186
				V_t	2·50	7·20	11·25	11·65	12·55
6	18·60	0·02770	0·02375	t sec.	97·2	326·0	664·6	1110	1328
				V_t	3·00	9·10	12·15	13·40	14·05
8	18·70	0·02770	0·02171	t sec.	107·8	296·8	540·4	769·6	973·5
				V_t	2·85	7·85	10·35	11·55	12·20
10	18·90	0·02704	0·02416	t sec.	118·6	380·5	639·9	908·6	1309
				V_t	4·10	9·95	12·25	13·45	14·45

TABLE VI

Alkaline hydrolysis of ethyl acetate in dioxan-water at 40° C.

% Dioxan by Volume	Titre of 10 ml. HCl	Concentration of OH′	Concentration of Ester		Titre value of aliquots				
0	20·35	0·02627	0·02322	t sec.	79·90	274·0	420·3	712·0	905
				V_t	6·70	12·50	14·20	15·80	16·00
2	18·45	0·02672	0·02448	t sec.	83·7	263·3	417·2	627·1	911·3
				V_t	6·40	11·50	13·20	14·40	15·25
4	19·90	0·02730	0·02265	t sec.	74·6	249·4	413·5	772·0	981·8
				V_t	5·50	11·15	13·15	14·85	15·30
6	19·25	0·02726	0·02645	t sec.	80·1	271·1	485·8	776·0	888·5
				V_t	6·85	12·70	14·90	16·20	16·50
8	19·85	0·02643	0·02476	t sec.	84·9	283·6	487·4	728·4	1003
				V_t	6·90	12·75	14·85	16·05	16·75
10	19·85	0·02730	0·02353	t sec.	75·9	223·8	394·4	654·7	924·8
				V_t	5·35	10·60	13·05	14·65	15·45

TABLE VII

The hydrolysis of ethyl acetate in the presence of potassium acetate

(The concentration of potassium acetate was 0·0444 M in all cases)

% Dioxan by Volume		Titre of 10 ml. HCl	Concentration of OH′	Concentration of Ester	Titre of 10 ml. HCl	Concentration of OH′	Concentration of Ester	Titre of 10 ml. HCl	Concentration of OH′	Concentration of Ester
Temp. ° C.			30			35			40	
0		19·10	0·0257	0·0262	19·10	0·0259	0·0254	20·35	0·0263	0·0232
2		19·20	0·0247	0·0254	18·60	0·0270	0·0261	18·45	0·0267	0·0245
4		19·10	0·0256	0·0245	19·30	0·0261	0·0224	19·90	0·0273	0·0227
6		17·75	0·0255	0·0244	19·15	0·0262	0·0246	19·25	0·0273	0·0265
8		17·90	0·0251	0·0263	18·40	0·0259	0·0233	19·05	0·0264	0·0248
10		19·10	0·0248	0·0248	20·95	0·0264	0·0265	19·85	0·0273	0·0235
30° C.	0	t sec.	117·3	326·1	533	785	1060	1254		
		V_t	4·85	10·25	12·65	14·40	15·40	15·90		
	2	t sec.	107·2	274·6	465·8	682·2	1244			
		V_t	5·25	10·10	12·50	14·15	16·15			
	4	t sec.	108·8	475·4	658·2	1084	1301			
		V_t	4·60	11·85	13·25	15·00	15·50			
	6	t sec.	105·2	316·6	527·1	725·4	1037	1324		
		V_t	3·80	8·95	11·25	12·60	13·65	14·30		
35° C.	0	t sec.	107·0	319·0	506·8	793·8	1069			
		V_t	5·10	10·85	13·05	14·75	15·65			
	6	t sec.	110·2	290·8	506·0	968·4	1373	1739		
		V_t	5·10	10·30	12·85	15·10	15·95	16·45		
40° C.	0	t sec.	79·9	274·0	420·3	712·0	906·1	1292		
		V_t	6·70	12·50	14·20	15·80	16·30	17·00		

The increased reaction rate in the region of small additions of organic solvents has then to be accounted for by the differences in the solvation of the proton and the transition state and the relative stability of the proton-oxygen bond. The anomalies have been noticed in the physical properties of these mixed solvents which are considered in a separate communication.

Experimental

The experimental technique was the same as in the previous Part. The dioxan used was a sample purified by the method of Eigenberger[4] the final purification being by fractional freezing. The physical constants of the solvent used were as follows:—

B.P. 100·5–100·8° C.; Density: d_4^{25} 1·02802; Refractive Index n_D^{25} 1·4202. Carbonate-free sodium hydroxide was used, freshly prepared each time and standardised before each experiment. The reaction was followed by changes in hydroxide ion concentration followed titrimetrically using an electrometric method employing the Serfass circuit indicated in the previous part. The temperature of the thermostat was maintained at the chosen level within a margin of 0·01° by electronic control together with efficient centrifugal stirring of bath.

Typical experimental runs are presented in Tables IV, V, VI and VII.

Summary

The kinetics of the hydrolysis of ethyl acetate by hydroxyl ions in dioxan-water systems also shows the same anticipated deviations from the Kirkwood picture of ion-dipole reactions. For small additions of organic solvents, more than the dielectric constant, the mole fraction of water and the changes in the environment of the transition state appear to be more significant. This is indicated by the reaction in the presence of acetate ions. The results are compared with those in acetone-water systems.

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40° C.	0	79·9	274·0	420·3	712·0	906·1	1292
	t sec.	6·70	12·50	14·20	15·80	16·30	17·00
	V_t						

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